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The 1982 Goddard Space Flight Center Battery Workshop

G. Halpert, Editor
Goddard Space Flight Center
Greenbelt, Maryland

A workshop held at
Goddard Space Flight Center
Greenbelt, Maryland
November 16-18, 1982

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PREFACE

This document contains the proceedings of the 15th Annual Battery Workshop held at Goddard Space Flight Center, Greenbelt, Maryland on November 16 to 18, 1982. The Workshop was attended by manufacturers, users and government representatives interested in the latest results in battery technology as they relate to high reliability operations and aerospace use. The subjects covered included Lithium Cell and Battery Safety Developments, Mathematical Modelling, Charge Control of Aerospace Power Systems, the Application of Nickel Hydrogen Cells/Batteries vis-a-vis Nickel Cadmium Cells/Batteries.

The Workshop comprised five separate Panel discussions on these subjects. This document contains the formal papers presented in each session, questions and answers, and a transcript of the discussion/comments by the attendees and panel members.

INTRODUCTION

Gerald Halpert
Goddard Space Flight Center

Welcome to Goddard Space Flight Center and to the 1982 Battery Workshop. We are pleased that this meeting continues to have the broad interest of those in the field of electrochemical power sources. I speak of the users, manufacturers and government technical representatives. For your interest, during last year's workshop, there were 53 attendees from 24 cell/battery manufacturing companies, 64 users from 22 companies, 51 government representatives from 17 organizations, 11 consultants and university personnel, and 43 others from miscellaneous interest groups. As far as territorial locations, 70 were local, 66 east coast, 32 midwest, 42 farwest and 8 foreign visitors. Goddard Space Flight Center (GSFC) is proud of the Battery Workshop. The Workshop continues to receive support from the attendees, from GSFC and NASA Headquarters Management.

We decided to take a different approach during this year's workshop, to help stimulate discussion. In the past, we have had terrific responses from those wishing to present technical papers, and these were appreciated. However, the word "Workshop" as defined by 'Merriam Webster' is: "...seminar emphasizing free discussion, exchange of ideas and practical methods, skills and principals, that is given mainly for those employed in the field." Therefore, a decision was made to change the format by allowing question-answer periods on selected controversial subjects. There are those who would say, for example, that the 'Lithium Safety' discussion is "old hat." The response I give to that comment is, that there are two issues: 1) the manufacturers desire to produce a safe, viable product, and 2) the concerns of the users for the safe operation of that product. The questions therefore, differ from those in the past, in that we are seeking more positive responses. Such as: Can it be made safe, and if so; How? It is also important to be aware of the problems. It has been said that this is the one meeting where these manufacturing/safety problems are discussed. I do not want to preempt Dr. Samuel Levy by any further discussion on this subject. I think you will note that the other subjects are also of a controversial nature and that we hope you will actively participate in the sessions on Modelling, Charge control, Reconditioning and Nickel Hydrogen versus Nickel Cadmium.

We are saddened at the loss of our friend Irv Schulman and wish to dedicate the session he was to chair (Session V) in his memory. Thank you all for your attendance, and thank you in advance for your participation.

PREVIOUS BATTERY WORKSHOP PROCEEDINGS PUBLICATIONS

For your information, we have included a list of the acquisition numbers for all Battery Workshop proceedings since 1970. Copies of previous publications are available upon request. The document numbers and the addresses are as follows:

<u>Year</u>	<u>Contents</u>	<u>Document Number</u>
1981	Workshop	82N20402
1980	Workshop	81N21493
1979	Workshop	80N20820
1978	Workshop	79N28669
1977	Workshop	79N21565
1976	Workshop	77N21550
1975	Workshop	76N24704
1974	Workshop	75N16976
1973	Workshop (1st Day)	75N15152
	Workshop (2nd Day)	75N17808
1972	Workshop (1st Day)	73N21956
	Workshop (2nd Day)	73N21957
1971	Workshop (Volume 1)	72N27061
	Workshop (Volume 2)	72N27062
1970	Workshop (1st Day)	71N28659
	Workshop (2nd Day)	71N28672

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CONTENTS
1982 Battery Workshop

General Chairman: G. Halpert, Goddard Space Flight Center

	<u>Page</u>
PREFACE	111
INTRODUCTION	v

SESSION I

TOPIC: CAN Li/SO_2 , Li/SOCl_2 , AND $\text{Li}/\text{SO}_2\text{Cl}_2$ CELLS BE MADE
SAFE ENOUGH FOR MILITARY, AEROSPACE, AND CONSUMER
USE?

Chairman: S. Levy, Sandia National Labs 1

Panel Presentations:

HAZARDOUS BEHAVIOR OF LITHIUM BATTERIES: CASE HISTORIES
N. Marincic, Battery Engineering, Inc. 3

THE GALILEO LITHIUM/ SO_2 BATTERY: THE SAFEST BATTERY ON
JUPITER
L. Marcoux, Hughes Aircraft 15

POLICIES GOVERNING THE USE OF LITHIUM BATTERIES BY THE NAVY
F. Bis, Naval Surface Weapons Center 23

A CONSUMER LOOKS AT LITHIUM BATTERIES
P. Bro, Consultant 35

Other Presentations:

FORCED OVERDISCHARGE RELATED SAFETY ASPECTS
K.M. Abraham, E.I.C. Laboratories. 47

CONTENTS (continued)

	<u>Page</u>
SAFETY TESTS	
P. Krehl, Electro Chem Industries.	60
LOW TEMPERATURE PERFORMANCE TESTS	
F. Goebel, General Telephone Electronics	64
CONTROLLING HAZARDOUS REACTIONS DURING VOLTAGE REVERSAL OF HIGH ENERGY LITHIUM CELLS	
M. Domeniconi, Altus Corp.	67
DESIGN OF A SAFE CYLINDRICAL LITHIUM/THIONYL CHLORIDE CELL	
D. Johnson, Union Carbide Corporation.	75
VALIDATING CELL/BATTERY SAFETY	
D. Chua, Honeywell	85
DISCUSSION.	100

SESSION II

TOPIC: MODELLING - IS THE EMPIRICAL OR SCIENTIFIC BASIS MORE RELIABLE AND USEFUL FOR PRIMARY AND SECONDARY CELLS?

Chairman: P. McDermott, Coppin State College 113

Panel Presentations:

BATTERY MODEL FOR ELECTRICAL POWER SYSTEM ENERGY BALANCE
 D. Hafen, Lockheed Missiles and Space Corporation. . . 117

MODELLING BATTERY LIFE THROUGH CHANGES IN VOLTAGE FIT COEFFICIENTS
 D. Fox and P. McDermott, Coppin State College 125

FITTING VOLTAGE CURVES WITH AN ELECTROCHEMICALLY DERIVED EQUATION
 M. Spritzer, Villanova University 164

CONTENTS (continued)		<u>Page</u>
MODELLING A LITHIUM-THIONYL CHLORIDE BATTERY FOR DESIGN PURPOSES		
D. Ernst,/D. L. Warburton, Naval Surface Weapons Center; A.S. Kushner, Anatech		178
<u>Other Presentations</u>		
COMPUTER MODELLING OF BATTERIES FROM NON-LINEAR CIRCUIT ELEMENTS		
I. Moskowitz, S. Waaben, and J. Federico, Bell Labs .		201
DISCUSSION.		216
SESSION III		
TOPIC: WHICH METHOD OF CHARGE CONTROL PROVIDES THE MOST RELIABLE OPERATION FOR NEAR EARTH OR SYNCHRONOUS MISSIONS?		
Chairman: S. Gross, Boeing Aerospace.		225
<u>Panel Presentations:</u>		
COMPARISON OF CHARGE CONTROL FOR FIXED ARRAY VERSUS SUN-ORIENTED MISSION		
G. Halpert, NASA/Goddard Space Flight Center.		230
BATTERY CHARGE CONTROL WITH TEMPERATURE COMPENSATED VOLTAGE LIMIT		
H. Thierfelder, General Electric.		259
ADVANCE BATTERY CHARGE AND CONTROL FOR FUTURE BATTERY SYSTEMS		
J. Masson, Martin-Marietta Corporation.		270
DISCUSSION		280

CONTENTS (Continued)

Page

SESSION IV

TOPIC: RECONDITIONING HAS SIGNIFICANT EFFECT ON BATTERY
LIFE: FACT OR FICTION?

Chairman: D. Pickett, Hughes Aircraft 293

Panel Presentations:

DEEP DISCHARGE RECONDITIONING: PROS AND CONS
W. Scott, TRW Systems 297

SPACECRAFT BATTERY RECONDITIONING COST CONSIDERATIONS
G. Van Ommering, Ford Aerospace 303

UNIQUE BATTERY RECONDITIONING CYCLE FOR RCA'S
GEOSTATIONARY SATELLITES AND ITS APPLICABILITY FOR
LOW EARTH SPACECRAFT
S. Gaston, RCA Astro-Electronics 311

RECONDITIONING AND THE NICKEL ELECTRODE
A. H. Zimmerman and C. Babcock, 324
Aerospace Corporation

Other Presentations:

STATUS OF SAFT SILVER HYDROGEN CELL DEVELOPMENT
P. Fougere, and J. Goualard, SAFT, France 347

DISCUSSION. 372

CONTENTS (continued)

SESSION V

TOPIC: DOES NICKEL HYDROGEN REALLY HAVE AN ADVANTAGE
OVER NICKEL CADMIUM?

Chairman: L. Slifer, Jr., NASA/Goddard Space Flight
Center. 385

Panel Presentations:

NICKEL HYDROGEN BATTERIES FOR COMMUNICATION SATELLITES
J. Dunlop, COMSAT Labs. 389

REAL AND POTENTIAL NICKEL HYDROGEN SUPERIORITY
F. Betz, Naval Research Laboratories. 416

NICKEL HYDROGEN: NICKEL CADMIUM TRADE-OFF STUDIES
S. Stadnick, Hughes Aircraft. 430

CANADIAN EXPERIENCE WITH THE NICKEL CADMIUM BATTERIES
J. Lackner, Defense Research Board, Canada 439

Other Presentations: 452

EXPERIMENT DESIGN
H. Lim, Hughes Research Labs 453

DETERMINATION OF THE RELIABILITY OF NICKEL CADMIUM BAT-
TERIES FROM SURVIVAL DATA ON CELLS FABRICATED 1964 to 1977
T. D. O'Sullivan, Bell Laboratories 470

ADVANCED NICKEL HYDROGEN CELL CONFIGURATION STUDY
E. Adler and F. Perez, Hughes Aircraft. 480

TEST METHODS AND RESULTS OF THE 10-CELL BIPOLAR NICKEL
HYDROGEN BATTERY
R. Cataldo, NASA/Lewis Research Center. 496

CONTENTS (continued)		<u>Page</u>
CHAIRMAN'S SUMMARY		
Luther W. Slifer, Jr., GSFC.		501
DISCUSSION.		502
LIST OF ATTENDEES		513

SESSION I

"CAN Li/SO_2 , Li/SOCl_2 , AND $\text{Li}/\text{SO}_2\text{Cl}_2$ CELLS BE
MADE SAFE ENOUGH FOR MILITARY, AEROSPACE, AND CONSUMER USE?"

S. Levy, Chairman
Sandia National Labs

HAZARDOUS BEHAVIOR OF LITHIUM BATTERIES

CASE HISTORIES

Nikola Marincic
Battery Engineering Inc., Hyde Park, Massachusetts 02136

ABSTRACT

Case histories were described of hazardous behavior for three different cell sizes ranging in nominal capacity from 300 mAh to 12,000 Ah. Design characteristics and other facts believed to have been responsible for the cell explosions, are presented to the audience as a background to the workshop discussion to follow. Obvious facts are discussed, alone or in combination with less discernible ones, as causes for hazardous behavior of lithium batteries in general and oxyhalide batteries in particular.

INTRODUCTION

Before we get involved in the discussion of details of the specific cases of hazardous behavior, let us state once more a few positive facts regarding the development of these, sometimes dangerous, batteries. Slide 1 illustrates the structure and the slide 2 shows the picture of a cardiac pacemaker, powered with two AA size lithium thionyl chloride cells, as they were developed and implanted first time in 1974. Four years and around 20,000 implants later no safety related problems were reported regarding this sensitive application of this potentially most hazardous battery system.⁽¹⁾ A look at the x ray of a more advanced version of the implantable cell on slide 3 shows that a well engineered low rate type cell can stand an extensive abuse without exhibiting any hazardous behavior. A $\frac{1}{4}$ inch steel ball was forced into a $\frac{3}{8}$ inch diameter cell sideways, disrupting the interior structure of the cell without even creating a short circuit. Shorted externally, such a cell would show only around 10°C increase in surface temperature with no sign of leakage or rupture throughout discharge.

At the other extreme of the size range, slide 4 shows a full size Minuteman Battery Module, as it was exhibited

publicly at the Atlantic City Symposium in 1980. 250 such batteries have been ordered this past summer by U.S. Air Force as a first phase of production at the new GTE plant at Henderson, Nevada (2). While the development of this power sources was quite dramatic, its present version appears quite safe thanks to careful engineering and a great respect with which this electrochemical system is being treated these days.

LARGE CELLS

Intentional abuse of large cells in course of development was a major source of information regarding the potential hazardous behavior. Slide 5 shows a 2,000 Ah cell after the short circuit discharge and the slide 6 illustrates the chronology of that short circuit test. A substantial energy was extracted from the cell in the first 40 minutes of the test before both the voltage and the discharge current dropped to a less dramatic level and before the cell pressure began to rise significantly. A steady increase in the cell case temperature was unimpressive throughout the test, leading to no rupture, leakage or explosion. The internal cell pressure dropped to a normal level upon cooling. The open circuit voltage was reestablished upon the removal of the load and, in spite of the dramatic change in shape, at no time did the cell exhibit any hazardous behavior.

The first full size cells of 12,000 Ah nominal capacity are shown in slide 7, as they were prepared for testing on site in 1976. The test data in slide 8 have been published previously (3) and the slide 9 shows five cell sub-modules after removal from the test site. One such cell, upon removal from the submodule case and in course of packaging for shipment, exploded, resulting in a tragic loss of life, as you all might remember. Six years after the accident, without claiming the full understanding of underlaying causes, with no intention of divulging sensitive information, placing no blame at any individual or organizations, and only in the interest of informing others still involved in similar developments, I shall list here some facts that in my opinion were relevant to this particular accident:

1. Around 7500 Ah out of the nominal 12,000 Ah have been extracted from this cell in course of the preceding test.
2. The cell was briefly open to the atmosphere at room temperature and 20-30% relative humidity, following the test, and the free electrolyte was drained,

2-3 days before the accident.

3. The major breakthrough in the technology of the electrolyte preparation came sometimes after this event, so that the electrolyte in this cell may have contained several hundreds ppm of hydrolysis products along with possible other impurities.
4. The hold-down fixture for the electrode structure, preventing relative motion of electrodes within the stack, has not yet been developed at the time of this accident.

STANDARD SIZE CYLINDRICAL CELLS

The most devastating explosion of standard size D cells I have ever investigated occurred within an oil well logging tool, in which lithium-thionyl chloride cells were arranged as partially shown in slide 10.

The most significant observations made during the investigation of this explosion are as follows:

1. Cells were made in nickel plated steel cases very similar to those used in Ni-Cd batteries.
2. The cell closing technique used was 1974 state-of-the-art involving a bearing ball and a resistance welder, as shown in slide 11.
3. A loose cathode - current collector subassembly was employed.
4. 900 ppm of hydrolysis products were found in the unused cells from the same batch.
5. Cells were less than 50% discharged prior to the accident.
6. All 28 cells blew up, presumably one after another in a fast succession, within a strong housing, shredding the housing itself. Parts of 24 cells were positively identified in the course of investigation and no undamaged cells were found.
7. The tool exploded at room temperature upon the removal of the end plug carrying a spring loading fixture that kept the cells together.

A more advanced design and the state of the art engineering were employed in the double D size cells shown in slide 12, intended specifically for oil well logging. The result of an external thermal abuse is illustrated in slides 13 and 14 for the top and the bottom, respectively. No leak through the glass seal was observed in spite of the extensive distortion of the cell cover assembly. The slide 15 shows the remains of the cell case following an explosion under external heating that was continued on purpose. No cell of this design could be made to explode under its own heat generated by the short circuit discharge.

MINIATURE CELLS

The smallest of cylindrical lithium thionyl chloride cells, made for the low power memory circuits, were abused extensively in an effort to cause their hazardous behavior. Short of the exposure to open fire, the only other consistent way to blow them up was by means of spot welding equipment. High pressure on the welding tip, combined with a high watt-second setting on the welding power supply, will blow up the cell every time, slide 16, with the physical discharge of all of the carbon and electrolyte and only a partial involvement of lithium anode.

Miniature button cells of a special design have been subjected to an extensive abuse testing. Slide 17 shows what an external thermal abuse could do to the shape of the cell without leading to the failure of this specially developed seal. However, the slide 18 will illustrate what an enterprising (or ignorant) user can do to make the best cells blow up. Being of such thin structure this cell will thermally equilibrate with the air stream from the heat gun within seconds, bulge into a sphere or blow up, depending how close to the heat source it has been placed. One such undertaking last year by a Navy contractor caused the cancellation of this most interesting project in spite of Navy's own praise for the cell design job well done (4).

SUGGESTED TOPICS FOR DISCUSSION

Based on the facts outlined in this presentation, related to one accident for each of the three groups of cells made with different levels of technological development, but with the same electrochemical system, I would like you, the audience, to consider possible causes for violent behavior of these cells. In particular, I am asking to hear various

opinions as to the cause or a combination of circumstances that might have been involved in the initiation of the explosion. Your thoughts should center around, but not be limited to, the following phenomena:

1. Hydrogen generation within a cell made with wet electrolyte.
2. Leaky closures combined with hydrogen accumulation in a closed system outside individual cells.
3. Loose electrode structures, sensitive to wear and tear under mechanical abuse.
4. Intermittent contacts within a loose electrode structure under mechanical abuse.
5. Intermittent intercell connections in a closed battery container, combined with a leaky cell seal and a hydrogen generation during discharge of cells made with wet electrolyte.
6. Exposure of cell interior to humid air and a nitride formation on lithium.
7. Presence of lithium nitride combined with a loose electrode structure and a mechanical abuse to nitride nuggets within lithium anodes.
8. Local overheating within a cell as a result of intermittent contacts within the electrolyte starved electrode structure.
9. Overheating and fusing of electrode interconnectors and/or cell interconnectors under excessive discharge current.
10. Shock propagation leading to the propagation of explosions from one cell to another in a closed system, combined with any or all of the other conditions mentioned above.

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1. M. Bilitch, PACE, Vol. 2, No 3, May 1979.
2. Boston Globe, 13 October 1982.
3. Proc. 28th Power Sources Symposium, Atlantic City, N.J. 1978.
4. Private communication, William H. Height, Naval Weapons Center, China Lake, California.

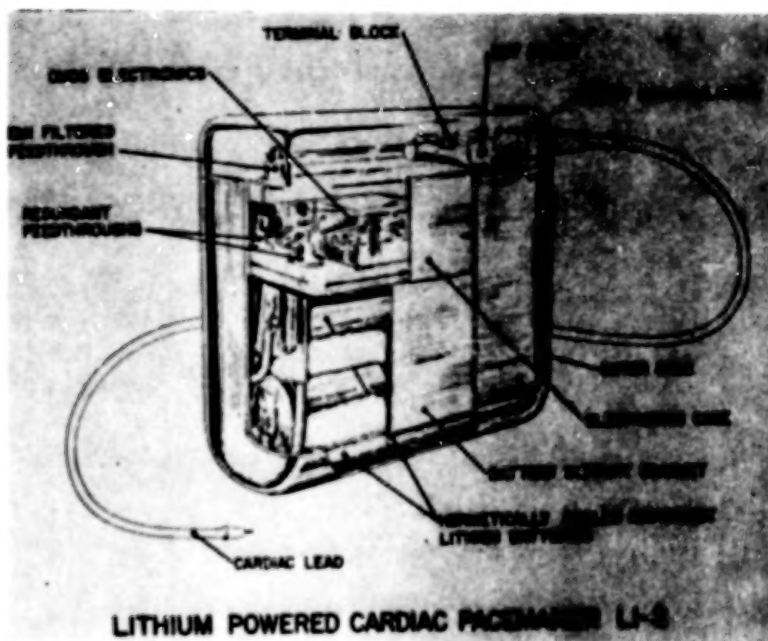


Figure 1 (Slide 1)

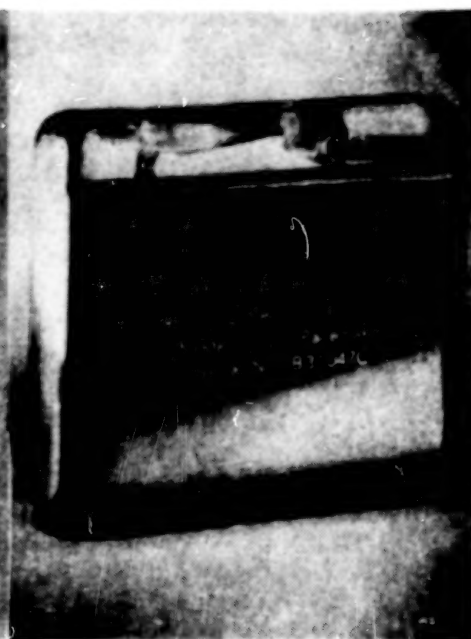


Figure 2 (Slide 2)



Figure 3 (Slide 3)

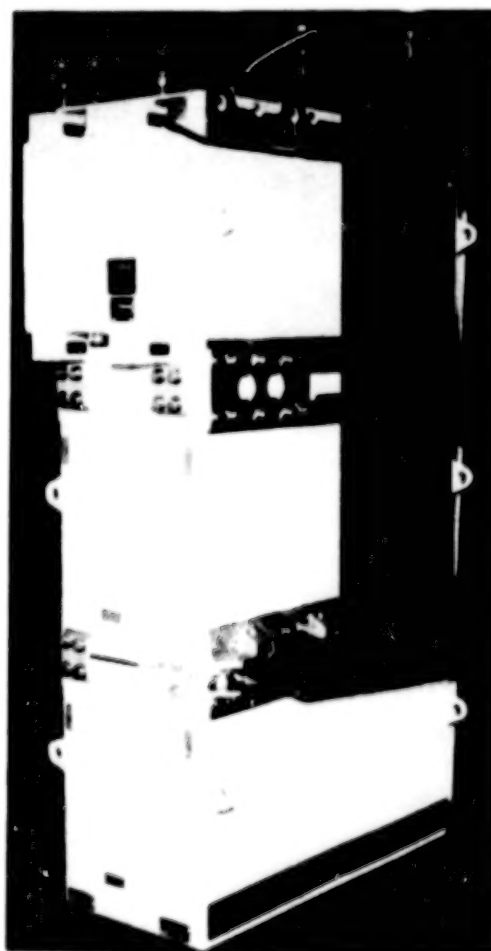


Figure 4 (Slide 4)

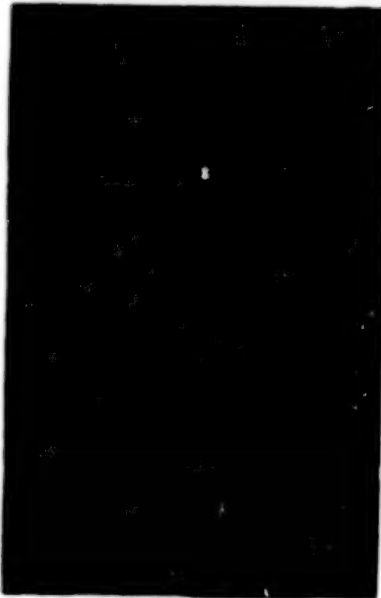


Figure 5 (Slide 5)

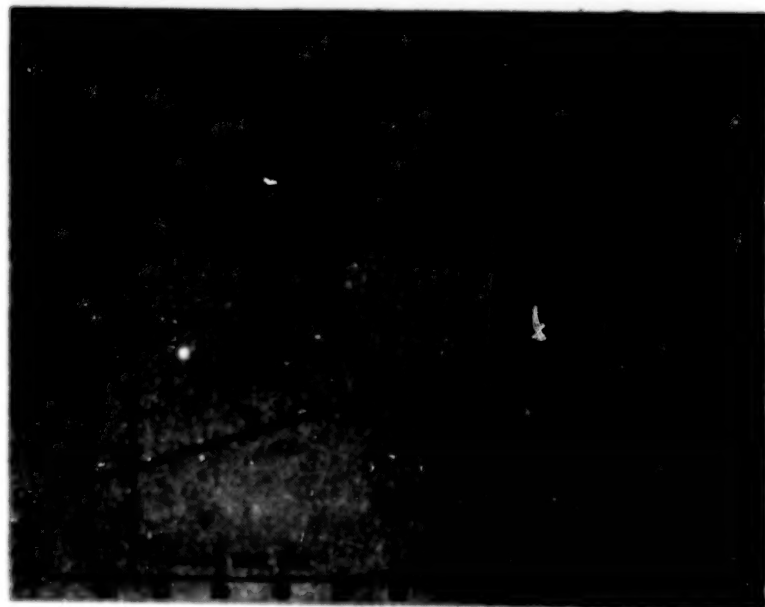


Figure 6 (Slide 6)



Figure 7 (Slide 7)

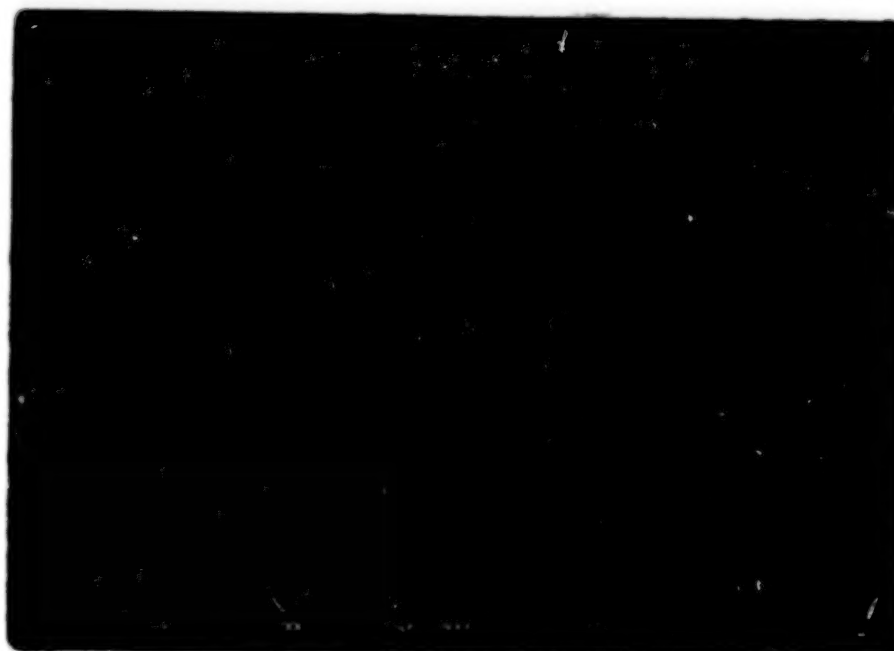


Figure 8 (Slide 8)



Figure 9 (Slide 9)



Figure 10 (Slide 10)

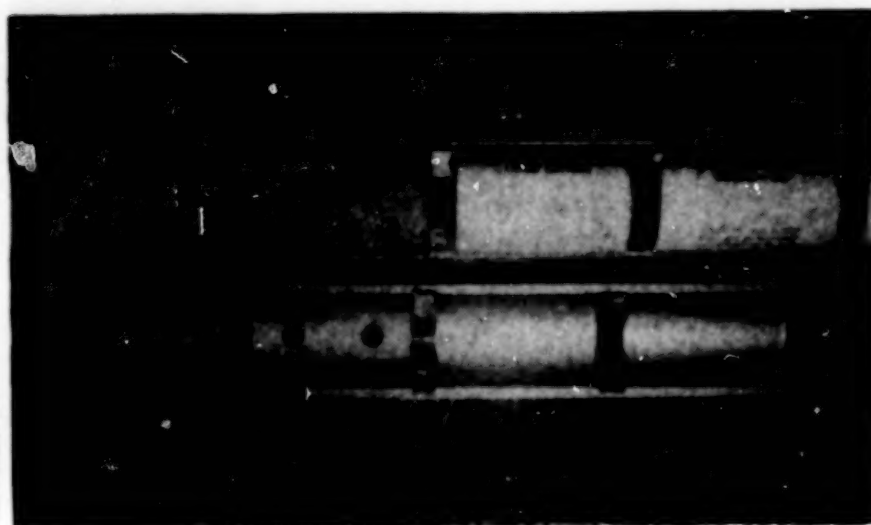


Figure 11 (Slide 11)

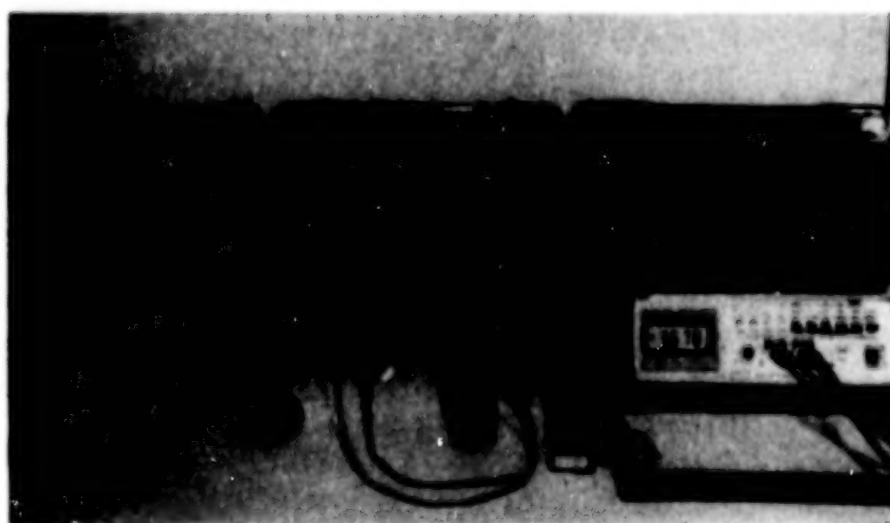


Figure 12 (Slide 12)

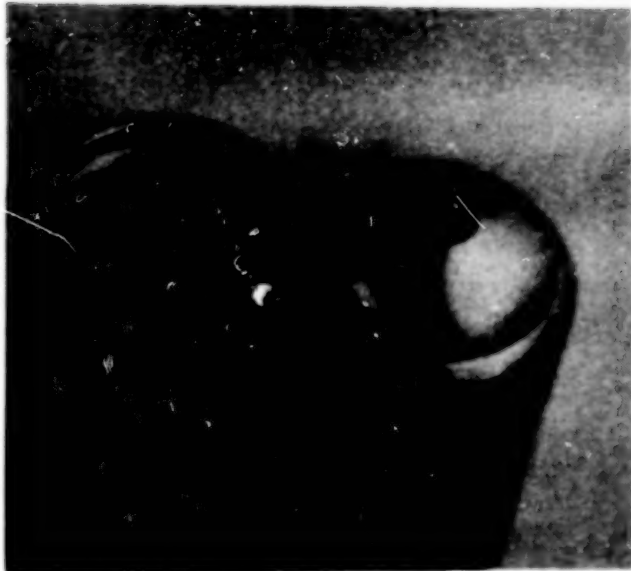


Figure 13 (Slide 13)



Figure 14 (Slide 14)

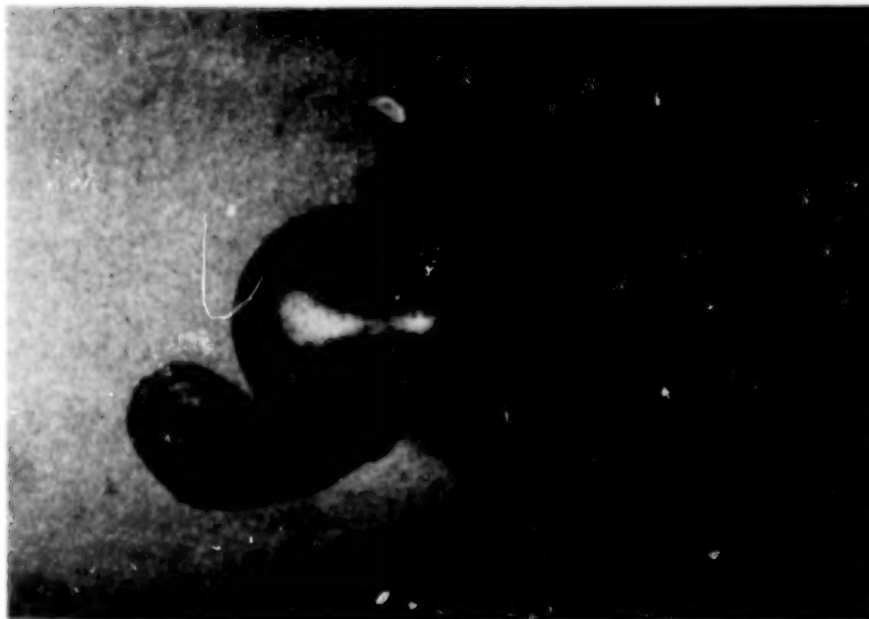


Figure 15 (Slide 15)

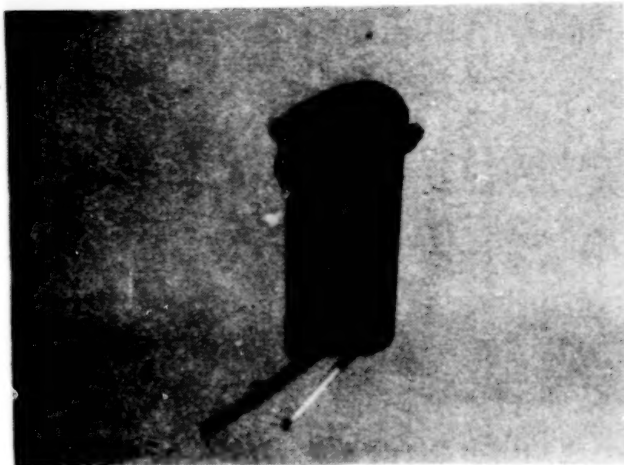


Figure 16 (Slide 16)

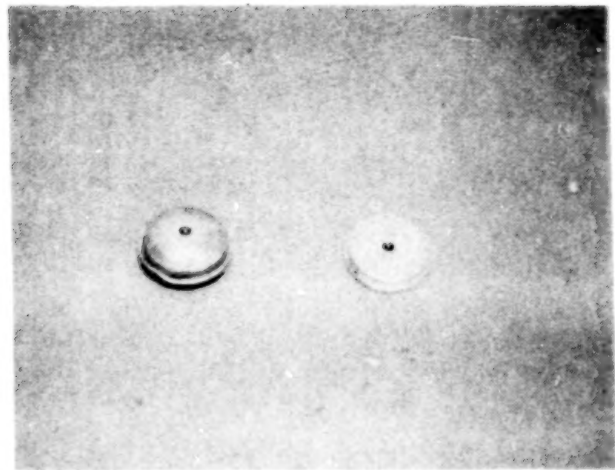


Figure 17 (Slide 17)

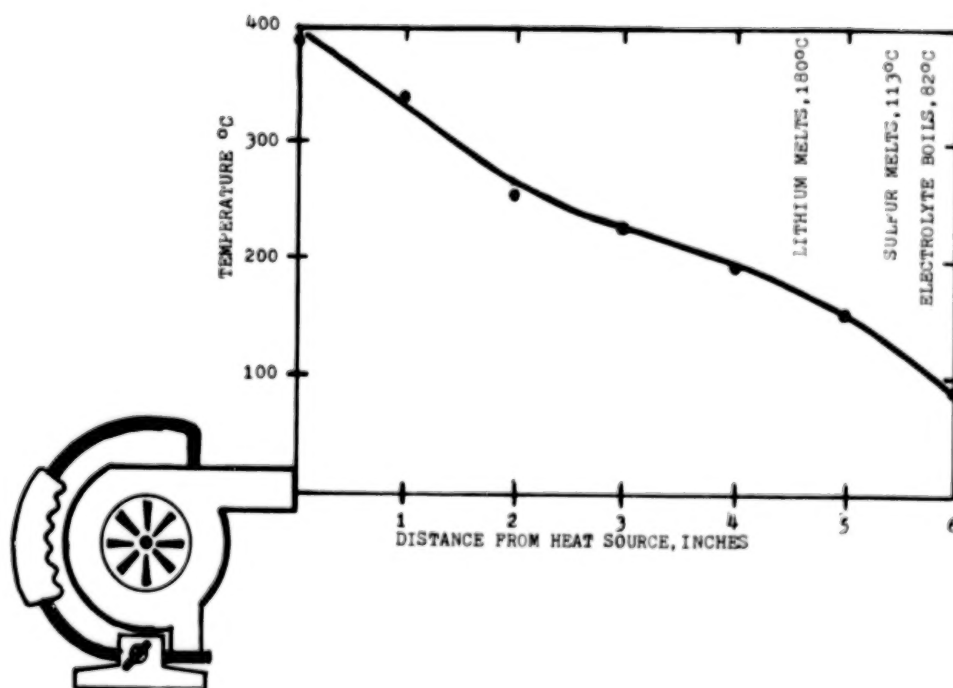


Figure 18 (Slide 18)

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THE GALILEO PROBE LI/SO₂ BATTERY

THE SAFEST BATTERY ON JUPITER

L.S. Marcoux and B.P. Dagarin
Space and Communications Group
Hughes Aircraft Company
El Segundo, California

ABSTRACT

The unique power requirement of NASA's Galileo Jupiter Probe are most readily met by a Li/SO₂ battery; however, because this battery system is not space-flight proven, extensive effort has been required to qualify this device from the stand point of performance and safety. Due to the rather checkered safety record of the Li/SO₂ system, safety has been foremost among the design considerations and has been addressed at the cell, battery and system level. The mission requirements which led to the choice of the Li/SO₂ battery and the safety engineering which went into the battery and power system design are described herein.

MISSION DESCRIPTION AND REQUIREMENTS

NASA's Galileo mission to Jupiter, to be launched by means of the STS in 1980, will consist of an orbiter and a probe, the probe being instrumented to descend through and analyze the Jovian atmosphere. All power for the probe will be supplied by three battery modules containing a total of 39 D-size Li/SO₂ cells which will be required to retain their capacity for the over 50 months of the mission and then provide current at the 3 to 4 A rate for 48 minutes.

The battery is quiescent until the probe separates from the orbiter, and from this point the load profile may be considered in three segments: 150 days of coast, 7 hours of pre-entry, and approximately one hour of descent. During the coast phase, one module provides a 30 mA pulse for 20 msec on top of a baseline current of 1.4 mA at an interval of 256 seconds. Also, during this period, three modules in parallel provide a 28 μ A current to the bus of an inertia switch which is the backup for the timer.

At the conclusion of the coast period, the battery is despassivated for 10 seconds by a 10-ohm resistive load which is followed by 10 additional seconds at 1.4A. During the remainder of the 6 hours by pre-entry, the battery provides 0.35 A to the spacecraft. the descent portion of the mission requires 10.3 A for approximately one hour. As well as this constant load, the battery must also support 30-msec pulses of 6.3 and 2.5 A which are required to initiate pyrotechnic events. The energy budget is summarized in Table 1.

The environmental requirements for the battery consist of conventional STS launch vibration and acceleration and the much more severe environments of deceleration and entry into the Jovian environment. The qualification deceleration requirement consists of a 425 g peak load followed by 30 seconds at 300 g in the z-axis. This is the spacecraft axis perpendicular to the long axis of the cells. The temperature profile seen by the battery followed launch is an interplanetary cruise temperature of 20°C after separation from the orbiter, and an entry and descent temperature beginning at -15°C and increasing to 60°C. During entry and descent the pressure increases from 0 to 16 Bars.

Due to the high instrument density of the probe, very little space is available for the battery modules, and this provides additional design constraints. As shown in Figure 1, the battery modules are fastened via brackets to two different electronic units.

During the study phase of the program two battery systems were considered, a hybrid alkaline system and a Li/SO₂ battery. The hybrid alkaline battery consisted of a 14 V, 20 Ah Cd/NiOOH unit designed to support the 150-day coast load and remotely activated Zn/AgO battery to provide power during descent. The weight and volume of the alternative hybrid alkaline battery are compared to the Li/SO₂ battery in Table 2. The weights shown in Table 2 do not include the charge/discharge control circuitry for the Cd/NiOOH coast battery which would be an additional weight penalty for the hybrid alkaline system. The Li/SO₂ system was selected based upon mission weight and volume constraints. The low temperature performance characteristics and projected 5-year shelf life were also important factors leading to the decision to space qualify a totally new type of primary battery. The fact that this battery system had not been previously used in space was mitigated to some extent by the large data base which had developed for military applications.

BATTERY SYSTEM DESCRIPTION

The basic battery element is a module which consists of 13 high rate D-cells fabricated specifically for the Galileo mission according to a strict manufacturing control document. These cells differ from more conventional cells in that the cathodes and anodes are 100% weight sorted to assure uniform capacity, the anode lead has been reinforced to withstand the launch vibration environment, the cell vent grooves have been 100% inspected to assure a narrow vent pressure envelope, and cells are individually numbered to assure traceability.

The battery module consists of 13 cells rigidly potted in place in an aluminum case designed to withstand the severe mechanical loads of entry deceleration. Cell interconnection within the battery is accomplished by means of a flexible printed circuit board upon which are mounted 13 bypass diodes which maintain the integrity of the cell string in the event of a single cell open circuit failure. The battery module is fitted with both a test connector which permits individual cell monitoring and a power connector for use in flight. The module is vented and cells are offset to permit proper functioning of the individual cell safety vents. Each module is provided with two thermistors to permit test and flight thermal monitoring. Figure 2 shows the finished module, Figure 3 a schematic top view and Figure 4, a detailed cross section of the module.

The three battery modules which constitute the probe battery operate in parallel during descent; however, during the 150 days prior to descent, a single module operates a timing circuit. The distribution of power is controlled by two power interface units, and all spacecraft loads are fused and/or current limited. The three modules are isolated from one another by either a relay in series with a diode or by two isolation diodes in series. A simplified schematic diagram of the battery is shown in Figure 5.

BATTERY SAFETY CONSIDERATIONS

Battery safety considerations are addressed at the power system, battery, battery module and cell level and are designed to be compliant with the requirements of NHB 1700-7A which delineates the safety requirements of all STS payloads. For hazardous functions this document requires that the payload must tolerate a minimum number of credible failures and/or operator errors determined by the hazard level. This criterion applies when the loss of a function or the inadvertent occurrence of a function results in a hazardous event. Hazards are defined as follows:

1. Critical Hazards. No single failure or operator error shall result in damage to STS equipment or in the use of contingency or emergency procedures.
2. Catastrophic Hazards. No combination of two failures, operator errors, or RF (radio frequency) signals shall result in the potential for personnel injury, loss of the Orbiter, ground facilities, or STS equipment.

The hazardous function in the case of the Li/SO₂ battery is cell venting caused by internal or external short circuits, high ambient temperature, cell reversal on cell charging. This hazard is viewed as critical rather than catastrophic.

At the power subsystem level this hazard is precluded by various fuses and diode and/or relay protection circuits. All major loads within the spacecraft are fused or current limited, the fuses being located at the unit or in one of the power interface units. Current limiting is always performed within the using load. The current limiting, if utilized, is designed to automatically preclude drawing (continuously) more than twice the normal current. In order to prevent the charging of a low voltage module by one of higher voltage all three modules are protected by a relay contact in series with a diode or with two diodes in series.

Safety features at the module level include a module case design which in no way can obstruct cell venting, cell bypass diodes which limit reversal voltages, and additional cell-to-cell isolation as provided by a rigid potting material. The cell bypass diodes are mounted in a flexible printed circuit board and also serve to increase system reliability in the event of a single cell failure. The flexible printed circuit board also serves de facto as a fuse since it cannot sustain the 30 to 50 A currents which would result from a hard external short.

The safety features of the cell are well known but bear repeating. These include:

- balanced stoichiometry
- hermetically sealed
- over pressure vent
- insulative cap
- insulative sleeve
- 100% lot acceptance test

Not only is the cell vented but the vent slot is 100% inspected and cell cases are rejected if the vent depth is not consistent with a blowout pressure of 300 to 725 psi as determined by an empirical calibration procedure. All electroactive components are 100% weight sorted which provide a high degree of capacity reproducibility thereby reducing the probability of cell reversal.

The compliance of the entire battery design to the safety standards for the use of Li/SO₂ cells is summarized in Table 3.

BATTERY TEST PROGRAM

In addition to design considerations related to safety the cells and modules have also been extensively tested in order to validate that design. The tests performed in the course of this program have included:

- High Temperature Test
- Sinusoidal Vibration Test
- Random Vibration Test
- Vacuum Thermal Cycle Test
- Ionizing Radiation Test
- 150 Day Coast Timer and G-Switch Load Test (Battery)
- Entry Deceleration Test
- Pressure Thermal Test
- High Pressure and Condensing Moisture Test
- Storage Test (0°)
- Descent Load/Temperature Profile Test (Battery)
- DOT Safety Tests
- Module Venting Test (to be performed)
- Cell Corrosion Tests

The highlights of this test program have been that all performance goals have been met and no internal short circuits or cell ventings (except in the case of the DOT tests where venting is required) have occurred. The only cell reversals experienced were early in the program near the end of mission simulation tests which utilized prototype cells.

CONCLUSION

The power requirements of the Galileo Probe Mission are best served by a Li/SO₂ battery which has been carefully designed for safety and performance. Three years of test results provide every reason to believe that this system will prove to be a safe and effective one.

Table 1. Mission Energy Budget

<u>ENERGY REQUIREMENT</u>	<u>CAPACITY, A-HR</u>
Ground Test	0.39
Storage Losses for 3.5 Years	2.10
Mission Loads	
Cost	4.88
Pre-Entry	2.74
Entry	7.81
Contingency	1.10
TOTAL	19.02

Table 2. Comparison of Candidate Battery Systems

System	Weight, lb	Volume, in ³
Li/SO ₂	13.5	230
Cd/NiOOH-Zn/AgO	29.4	493

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Table 3. Summary of Battery Design Compliance to Safety Standards

<u>LEVEL</u>	<u>DESIGN GOALS*</u>	<u>GALILEO PROBE BATTERY DESIGN</u>
Cell	Balanced or Li limited	Balanced
Cell	Hermetically sealed and vented	Each cell contains a vent and is hermetically sealed
Cell	Vent device not blocked	Module opening at each vent (100% inspection)
Cell	Do not charge cells	Three inhibits in system
Cell	Do not short across header from (+) to (-)	Insulative cap on header
Cell	Cull defective cells	100% Lot Acceptance Test
Cell	Temp: Long term storage $\leq 45^{\circ}\text{C}$ Short term storage $\leq 60^{\circ}\text{C}$	0°C Ground, 20°C orbiter Launch $\leq 50^{\circ}\text{C}$
Cell	Each cell insulated from other	Module provides double insulation
Battery	Fuse battery (+) and (-) busses	Load fusing (see Figure III-I)
Battery	Parallel Module isolation	Relay + Diode
Battery	Cell By-pass diodes	Contained in Model circuitry
Battery	Suggests Thermal Switch set at 85°C	None
Battery	Cut-off volt equal to 2.0V/cell	System uses battery slightly beyond this level at end of mission
Battery	Avoid cell-cell contact	Double Insulation
Battery	Contain or vent products	Vented case

*From Lithium-Sulfur Dioxide Cell and Battery Safety Handbook, GHB 1710.5, 12 June 1981.

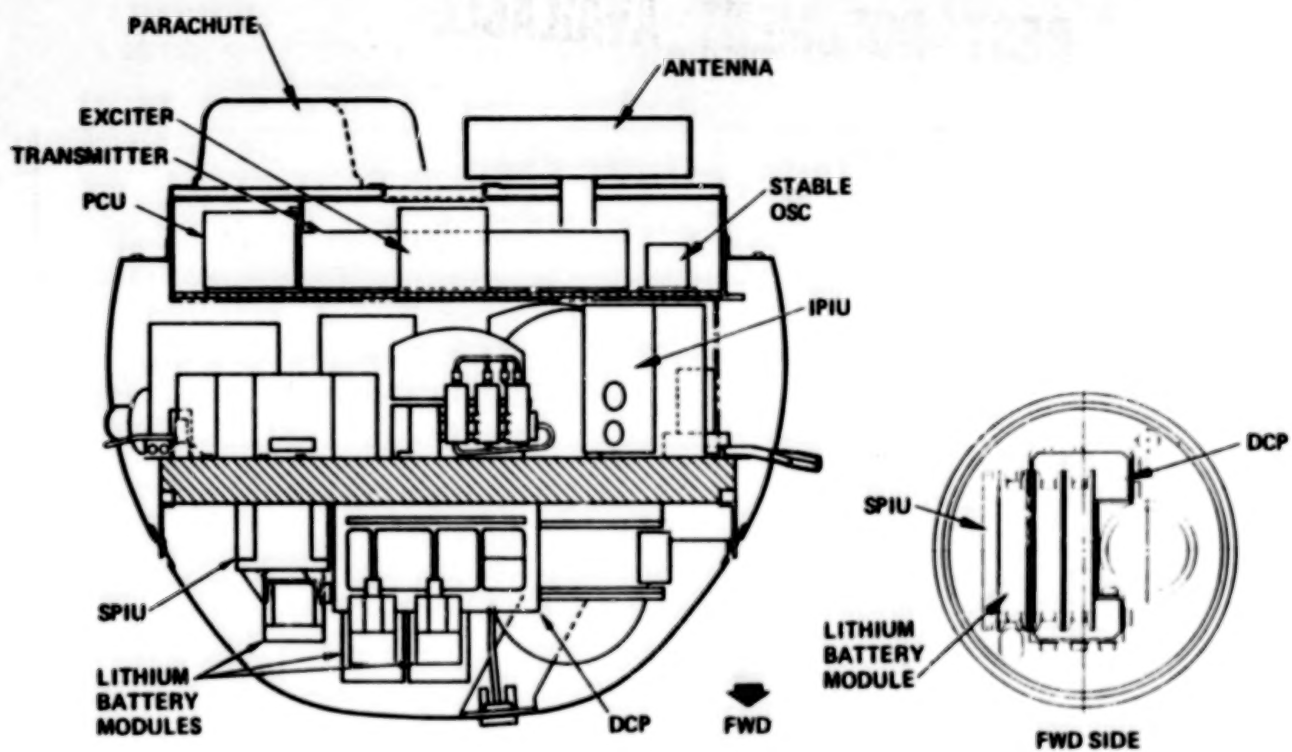


Figure 1

Li/SO₂ BATTERY MODULE

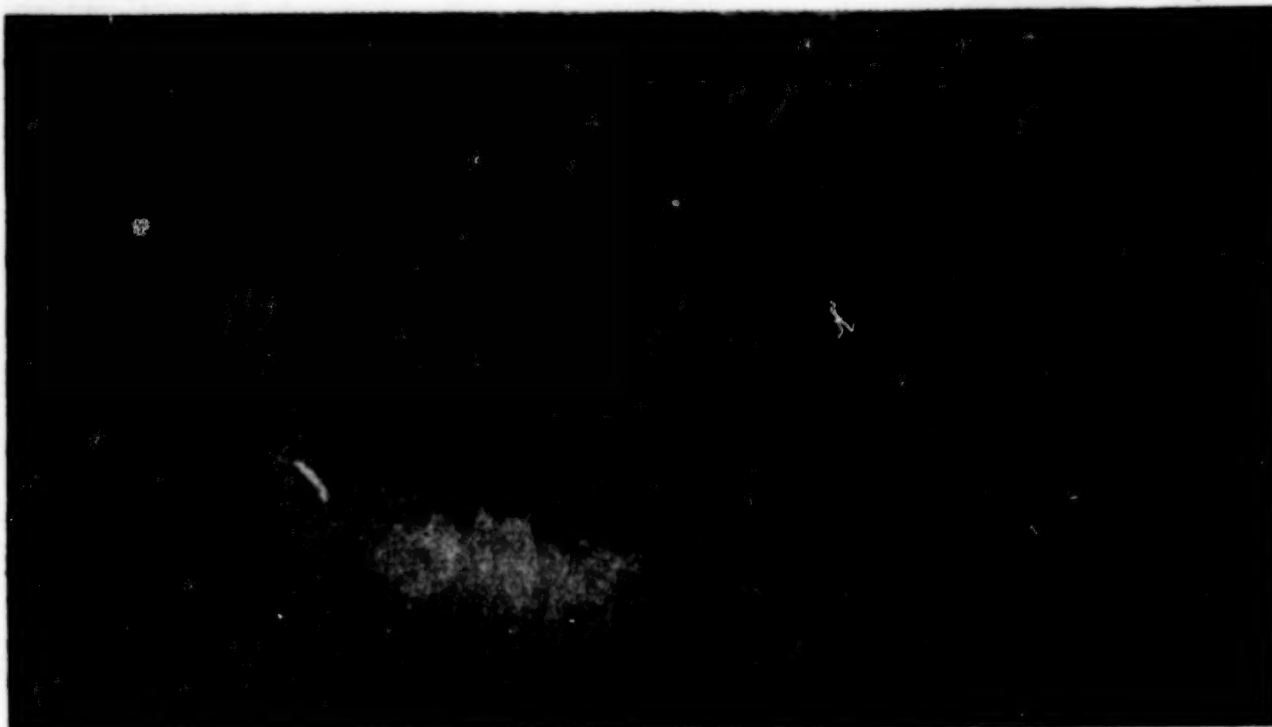


Figure 2

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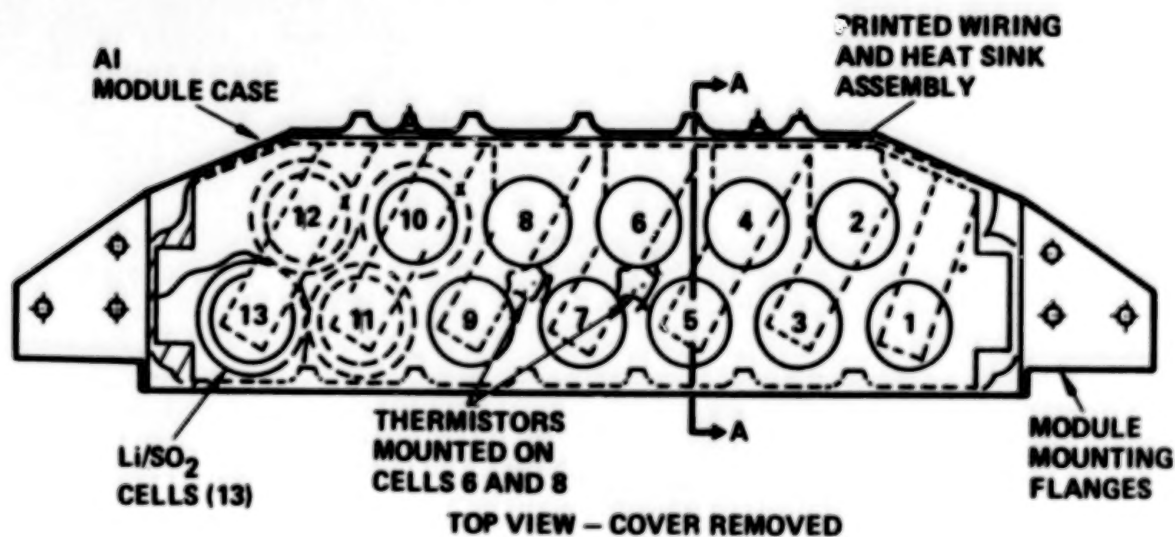


Figure 3

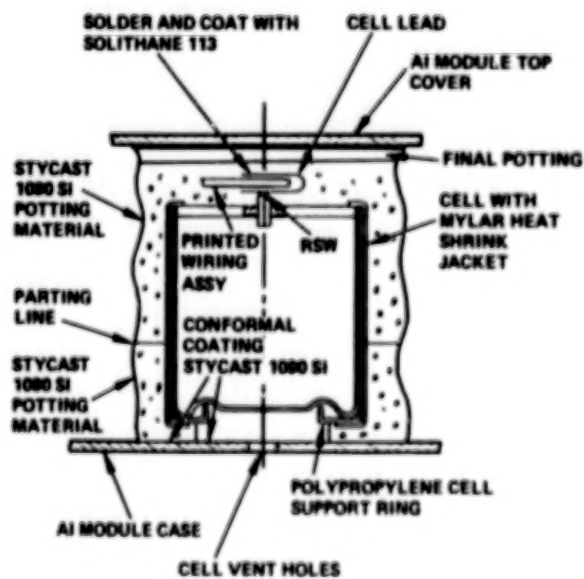


Figure 4

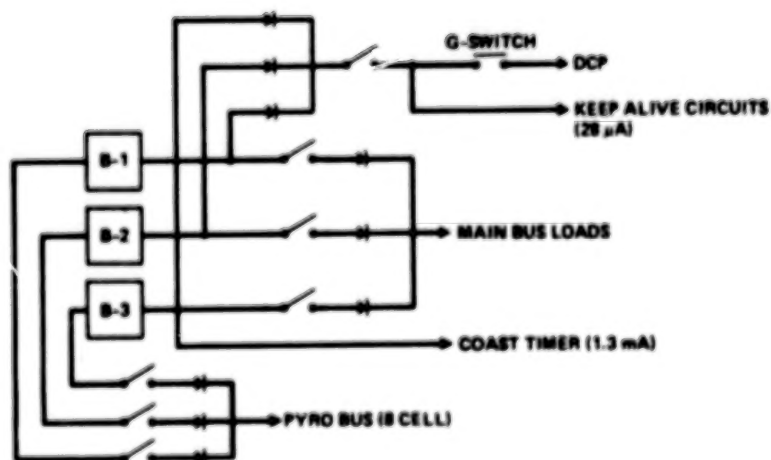


Figure 5

POLICIES GOVERNING THE USE OF LITHIUM BATTERIES IN THE NAVY

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ABSTRACT

Lithium batteries offer many advantages for Navy systems but may also exhibit undesirable hazardous behavior. Safety problems have been traced to a variety of chemical and physical causes. The Navy has established a central safety office with responsibility for all lithium battery use. Before an item is approved for Navy use, it must pass both a design review and a set of end-item tests. These reviews focus on complete systems composed of battery inside the end item. After system approval, specific regulations govern the transportation, storage, and disposal of the unit containing lithium batteries. This paper discusses each of these areas in detail.

INTRODUCTION

The purpose of this paper is to present a brief overview of the policies which govern the use of lithium batteries in the Navy and to discuss how these policies are implemented. The Navy does not have an official position with respect to the use of lithium-containing batteries in commercial applications.

LITHIUM BATTERY PROPERTIES AND HAZARDS

Lithium electrochemical systems have several properties which make them very attractive for many applications including the following items:

1. High energy density per unit weight and volume
2. Excellent voltage regulation
3. The ability to operate over a relatively wide temperature range
4. The ability to be discharged at high rates
5. Protected long storage life without the need for refrigeration.

The hazards associated with lithium electrochemical systems include

1. Explosions
2. Venting of toxic gases, often at high pressures
3. Fires
4. Disposal.

*On assignment from Austin College to NSWC under an Intergovernmental Personnel Act appointment

The first three items are clearly problems, but is it appropriate for disposal to be on this list as well? Lithium batteries must be disposed of as reactive hazardous waste. As such, the person signing the disposal order remains forever responsible. Another way of looking at this disposal problem is to say that you cannot contract away your responsibility. As long as waste lithium batteries are classified in the above manner, their disposal will be a non-trivial problem even if the other dangers listed can be minimized.

Hazardous behaviors such as exploding, and venting, have been traced to a variety of causes, including the following:

1. Short circuits
2. Discharge rates in excess of design
3. Forced overdischarge
4. Charging
5. Heating (fire)
6. Deterioration of the glass to metal seal
7. Improper vent operation
8. Undefined chemical reactions/products associated with some use conditions.

The Navy's concern about the need to exercise due care in the use of lithium batteries is reinforced by the history of accidents which have accompanied their use. Figure 1 is a list of some of these incidents. Some progress is being made in identifying and minimizing possible causes of accidents. For example, many of the early problems mentioned in the list were caused by zinc/sulfur dioxide cells which were not hermetically sealed. This mode of failure has been eliminated by the introduction of hermetically sealed cells. It is our hope that basic research in combination with careful attention to design details will allow us to continue to minimize the risks associated with the use of lithium batteries.

BASIC NAVY POLICY

The basic policies for the use of lithium battery powered equipment in the Navy are governed by Reference 1. The implementation of this instruction will be discussed in the remainder of this paper. The first premise of this instruction is that lithium batteries are to be considered for use only when no other form of power supply will satisfy the scenario of use of the system being designed. If the absolute need for a lithium electrochemical system can be clearly demonstrated, then the Navy may allow its use after extensive processes of design review and testing on the battery and the end item as a unit. Naval approval is limited to the approval of the end item and battery. The Navy has never given a "general" approval to any electrochemical system or cell.

The Navy has tasked (Ref. 1) NAVSEA 06H* and the Electrochemistry Branch (R33), Naval Surface Weapons Center, with the responsibility for

*The code of this office was NAVSEA 04H until recently.

lithium battery safety under the guidance of the published instruction. This approach provides the Navy with a central point of review for all systems containing lithium batteries.

DESIGN CONSIDERATIONS

The review process begins in the early stages of equipment development and continues until an item is approved for service use. The review process is typically divided into two stages: a preliminary review during the design phase and a final series of tests done prior to making a decision about general Navy use.

Prior to NAVSEA Instruction 9310.1A, equipment was developed by a manufacturer without an explicit, coordinated safety program and delivered directly to the Fleet. When a variety of safety problems prompted the Navy to establish a central safety office, technological fixes were added to designs which were already under development, and in some cases, were already in production. This approach has allowed the Navy to be more confident about the safe operation of the lithium battery equipment in the Fleet, however, such an approach is often expensive and can impact on Fleet readiness. We are now beginning to realize our goal of a coordinated R&D program in which the scientific and technological data available through the safety office are applied early in the design phase so that retrofits are not required.

The preliminary safety review is a paper review which focuses on issues such as where and by whom the equipment will be used, power and discharge requirements, and the proposed design of the battery and associated equipment. This review often results in recommendations for design changes to improve safety. Once sample equipment is available for testing, tests may be run to confirm the conclusions reached during the preliminary review. This preliminary testing sometimes results in further modifications prior to the letting of a production contract. A final, extensive test program is required before an item will be recommended for Fleet use.

These reviews and tests are shown schematically in Figure 2 and will be discussed in more detail in the following sections.

BATTERY DESIGN AND FUSING

Some of the more common circuits encountered in the Navy are shown in Figure 3. Note that both thermal and electrical fuses are recommended. These fuses are normally placed in the ground lead in order to prevent a short circuit from occurring if a cell case were to rub against a grounded housing. If these fuses were placed in the hot lead, any contact between a cell case and ground would cause a short circuit which would bypass the fuses. Such a short circuit could lead to a runaway electrochemical reaction with subsequent cell failure through explosion, fire, and/or venting.

If the battery includes parallel strings, diodes must be installed to prevent one string from charging another string. Similar protection against accidental charging is also required if the battery is to be used in equipment which is attached to some other source of electrical power such as a bus bar.

Once the battery circuit is approved, then its physical design is reviewed to insure that the fuses and vents are properly placed. No aspect of battery assembly (such as the use of potting material or glue) may interfere with the pressure relief vents which are part of most cells.

END ITEM HARDWARE DESIGN

The design review extends beyond the battery to include the equipment in which it is to be used and includes both electrical and physical factors. All battery support brackets should be insulated and all electrical wiring well protected and routed to prevent shorting. The battery and its support system must be designed to survive the shock and vibration typical of use including transportation by road, air, or sea, as well as accidents such as dropping. Some equipment must also survive more extreme shocks such as those associated with an air drop or gun launch. Because it is possible for batteries to fail and vent in spite of the safety measures mentioned, the equipment must be designed so that such a venting does not result in additional hazards. For most equipment, this requirement means that a pressure relief pathway be present so that the peak pressure in any incident will be less than half the yield point of the unit. If lithium-powered equipment is to be used aboard a submarine, it should be designed so as to contain all the venting products.

TEST PROGRAMS

The Navy is currently engaged in two types of testing involving lithium batteries. A continuing effort is made to evaluate new battery systems as they are developed, before they are adopted as part of any Navy equipment. A separate safety test program has been established to confirm that every end item containing lithium batteries is appropriate for use in the Fleet.

BATTERY TEST PROGRAMS

The first of the two test programs mentioned is designed to provide basic data about new electrochemical systems. This program provides background information about both performance and safety to the application engineers who choose a specific battery for a piece of equipment. Such a test program often begins with a study of a battery's construction using tests such as X-ray and careful disassembly and component analysis. The information gained from this analysis in combination with data provided by the manufacturer allows us to estimate the probable performance characteristics of the battery.

These characteristics are evaluated through an extensive set of tests including open circuit voltage; discharge under a variety of pulsed and

constant loads; shock and vibration testing at low, ambient, and elevated temperatures; and studies of the effect of storage at a variety of temperatures on both voltage delay and total capacity. Batteries are also subjected to testing in order to understand any safety hazards which might be associated with abuse in the field. These tests include short circuits, forced discharge into voltage reversal, charging of fresh and discharged batteries, and heating the batteries to 500°C. Other tests may include crushing or penetrating the battery (as with a nail) and heating the battery to produce a local hot spot. As a result of several recent incidents, in which a construction detail led to battery failure, we expect to develop additional abusive tests which will focus on any unusual features of a battery design which might produce hazards unique to the design.

There is no question that every battery will fail under some or all of these tests. The abusive tests are designed to characterize the nature of the failure in order to assess its effect on safety. For example, some small, low-rate cells can undergo the full test program without rupturing the cell case while certain high-rate batteries have exhibited a tendency to detonate under almost any form of abuse.

When it has been found that a battery will vent under one or more conditions of abuse, then additional tests are run to determine the nature of the gases released. To accomplish this analysis, batteries are forced to vent in a sealed vessel. Samples of the gas are collected for further analysis, most frequently by gas chromatography/mass spectrometry (GC/MS) methods. Given the composition of the gas and its temperature, pressure, and volume we can estimate the effect the gas would have on a person if the batteries were to vent in an open or closed room.

TEST PROGRAM FOR COMPLETE UNITS

Reference 1 prescribes a specific test program for all equipment containing lithium batteries after it has passed design review and before a safety recommendation on Fleet use is made by NSWC to NAVSEA 06H. This test program consists primarily of abusive tests and is characterized by two distinct features:

1. Complete pieces of equipment are tested in order to evaluate not only the safety hazards of the battery per se, but also any additional hazards produced by the unit surrounding the battery.
2. Tests are designed to provoke "worst case" failures for each form of abuse.

The requirements for the testing of complete units is based on the observation that the failure mode for a piece of equipment may depend upon subtle design features other than the battery itself. For example, in a recent study of buoys (Ref. 2), two buoys contained slightly different batteries assembled by the same manufacturer using the same basic cells. One of these buoys passed the safety review while the other failed because the sonobuoy flew apart when its battery was abused. "Worst case" testing

allows us to gain an understanding of the maximum hazards associated with a unit while testing a minimum number of units. When the test results are evaluated, an effort is also made to estimate hazards under less than worst case conditions.

Passing criteria have been established for the behavior of a unit under battery abuse as a function of where the equipment is to be used.

For use on land the unit must contain a fail-safe vent system such that the internal pressure of the unit never exceeds 50% of its yield point.

For use on aircraft and surface ships, the land requirement is supplemented with a further limitation that battery failure produce no external fire or flame.

For use on board a submarine, the unit must be designed to provide total containment with a maximum internal pressure less than 50% of the failure pressure of the housing.

Although these criteria have been defined as passing, a failure of equipment powered by lithium batteries to meet a criterion does not always result in an automatic rejection of the equipment for service use. Items which fail to meet a criterion will be rejected only if a technical evaluation of the test results by NAVSEA 06H establishes that rejection is the appropriate course of action.

Test Program

A typical test program consists of subjecting three units to each of three forms of abuse, for a total of nine tests.

Instrumentation - During each test instrumentation is used to continually monitor the battery voltage and current, the temperature of the battery and surrounding equipment, and the pressure inside the equipment. A minimum of six thermocouples are used to measure the temperature at the middle and each end of the battery pack, in the air space near the battery, and on the outside of the unit. A pressure transducer is used to measure the pressure inside the battery pack housing.

Constant Current Discharge and Reversal Test - In this test, all internal fusing is bypassed and the battery is discharged at a constant current equal to the battery fuse value using a DC power supply. The voltage of the power supply should be limited to the open circuit battery voltage. After the battery reaches zero volts, it is discharged at the same current into reversal for a time equivalent to 1.5 times the advertised ampere hour capacity of the battery pack.

Short Circuit Test - This test consists of shorting the battery (after all internal electrical safety devices have been bypassed) through a load of 0.01 ohm or less until the battery fails or 24 hours have passed.

High Temperature Test - This test consists of heating the battery pack inside the unit at a rate of 20°C per minute to a temperature of 500°C. Heating is normally done by wrapping the battery pack with electrical heating tape.

Charging Test - If a battery contains parallel strings or is attached to a source of external current, then an additional set of tests is required. In these tests all protective diodes are bypassed, the battery is discharged to at least 75%, and then it is charged at a current equal to the fuse value to 100% of its rated capacity. The results of these tests are evaluated using the criteria discussed earlier. The voltage of the power supply should be limited to the open circuit voltage of the battery.

STORAGE OF LITHIUM BATTERIES

Specific policies have been adopted to govern the storage of new and used lithium batteries.

NEW LITHIUM BATTERIES SHALL BE STORED AS FOLLOWS:

1. Lithium batteries shall be stored in their original shipping containers in a cool, sprinkler-protected ventilated shelter.
2. The storage area shall be isolated from other hazardous and combustible material and used only for the storage of unused lithium batteries.
3. Since the effect of mass storage on the hazard degree is not known, the quantity stored in an area shall be kept to a reasonable minimum.
4. Batteries in storage shall be retained in unit packages, preferably shipping containers, to prevent heat transfer between batteries.
5. Storage temperature above 130°F shall be avoided.
6. Special care shall be exercised in handling and moving containers to prevent crushing or puncturing.

USED LITHIUM BATTERIES SHALL BE STORED IN THE FOLLOWING MANNER:

1. Used lithium batteries shall be individually sealed in a plastic bag or be individually wrapped in electrical insulating material and be placed in Department of Transportation approved shipping container in accordance with 49CFR13.200.
2. A remote collection point and storage area, sprinkler protected (if feasible), separate from other combustible material shall be established for batteries awaiting disposal.

3. Used lithium batteries shall not be allowed to accumulate and disposal shall be effected promptly (no more than 30 pounds or 30 days).
4. Lithium batteries are not to be disposed of nor transported with normally generated refuse.
5. Used lithium batteries shall not be pierced, crushed, burned, dropped, cannibalized, dismantled, modified, or otherwise carelessly handled. Nor shall they be short circuited, charged or reused.

When entering a storage space in which lithium batteries may have vented gas, supplied air respirators or self-contained breathing apparatus approved by the National Institute for Operation Safety and Health (NOISH) shall be worn.

TRANSPORTATION

Transportation of both new and used batteries are governed by Federal regulations relating to shipment of hazardous materials. The general regulations are published in 49CFR172.101, 173.206(E)(L) and 175.3. The Materials Transportation Bureau, Research and Special Programs Administration, U. S. Department of Transportation, Washington, DC 20590, has issued exemptions to allow the shipment of lithium cells and batteries if detailed requirements regarding cell size, test results and packing are met. Fresh batteries, alone or in equipment, may be shipped by motor vehicle, rail freight, cargo vessel, and cargo-only aircraft, under Exemption DOT-E-7052. Any company or group shipping under this exemption must be explicitly registered with the Department of Transportation prior to shipping batteries by any mode. Exemption DOT-E-8441 permits the shipment of waste lithium batteries to a disposal site only by motor vehicle.

DISPOSAL

Navy regulations covering the disposal of new or used lithium batteries are based upon the applicable regulations of the Environmental Protection Agency. At sea, batteries are disposed of by discharge overboard in deep water (in excess of 500 feet) outside the prohibited zone (50 mile limit). This method of intentional disposal mimics the fate of batteries used in Navy systems at sea where the equipment is not normally recovered. Ashore, batteries may be disposed of by turning into the nearest public works center for disposal by the Defense Logistics Agency (DLA). The DLA is in the process of arranging to collect and to dispose of waste lithium batteries being held by all the military. Although a final decision has not been announced, this collection and disposal will probably be done by an outside contractor.

SUMMARY

In order to facilitate the use of lithium batteries with minimum risks to property and personnel, the Navy has established a central point of contact for safety reviews under the guidance of NAVSEA INST. 9310.1A. The safety review of a particular unit is composed of several distinct steps each of which contains defined tests. The review is guided not only by the test results but also by additional information gained from basic research and from consultation with other laboratories in both government and industry.

At the end of this presentation at the Goddard Battery Workshop Conference, a video tape of selected tests of lithium batteries was shown.

REFERENCES

1. NAVSEA INSTRUCTION 9310.1A, Naval Lithium Battery Safety Program; responsibilities and procedures for; 11 March 1982.
2. R. F. Bis, D. L. Warburton, L. A. Kowalchik, J. D. Jensen, G. F. Hoff, and C. A. Freeman, "Safety Evaluation of AN/SSQ-62 Sonobuoys Manufactured by MAGNAVOX, RAYTHEON, and SPARTON", NSWC/WO TR 82-36, 2 February 1982.

























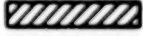





























DATE	PLACE	VENTING	FIRE	EXPLOSION	DAMAGE	
					STRUCTURE	PERSONAL
OCT. 1974	MIAMI, FLA.					
OCT. 1974	CHICAGO, ILL.					
NOV. 1974	CHICAGO, ILL.					
NOV. 1974	SEATTLE, WA.					
AUG. 1976	--					
AUG. 1976	HILL AFB					
DEC. 1976	FT. MONMOUTH, N.J.					
FEB. 1977	COSTA MESA, CA					
FEB. 1977	MINNEAPOLIS, MINN					
MAR. 1977	WAYNARD, MA.					
JULY 1977	NORWAY					
JULY 1967	LANGLEY VA.					
JULY 1979	HORSHAM, PA					
JUNE 1979	BERMUDA					
SEPT. 1979	BERMUDA					
SEPT. 1979	HIGH SEAS					
JUNE 1980	NORWAY					
JAN. 1981	FORT BRAGG					
JAN. 1981	FORT SILL					
FEB. 1981	FORT MEAD					
APRIL 1981	FORT HUACHUCA					
NOV. 1981	GERMANY					
NOV. 1981	CHINA LAKE					
FEB. 1982	NWSC					
FEB. 1982	NWSC					

Figure 1

**SAFETY REVIEW INTERACTIONS UNDER
NAVSEA INSTRUCTION 9310.1A**

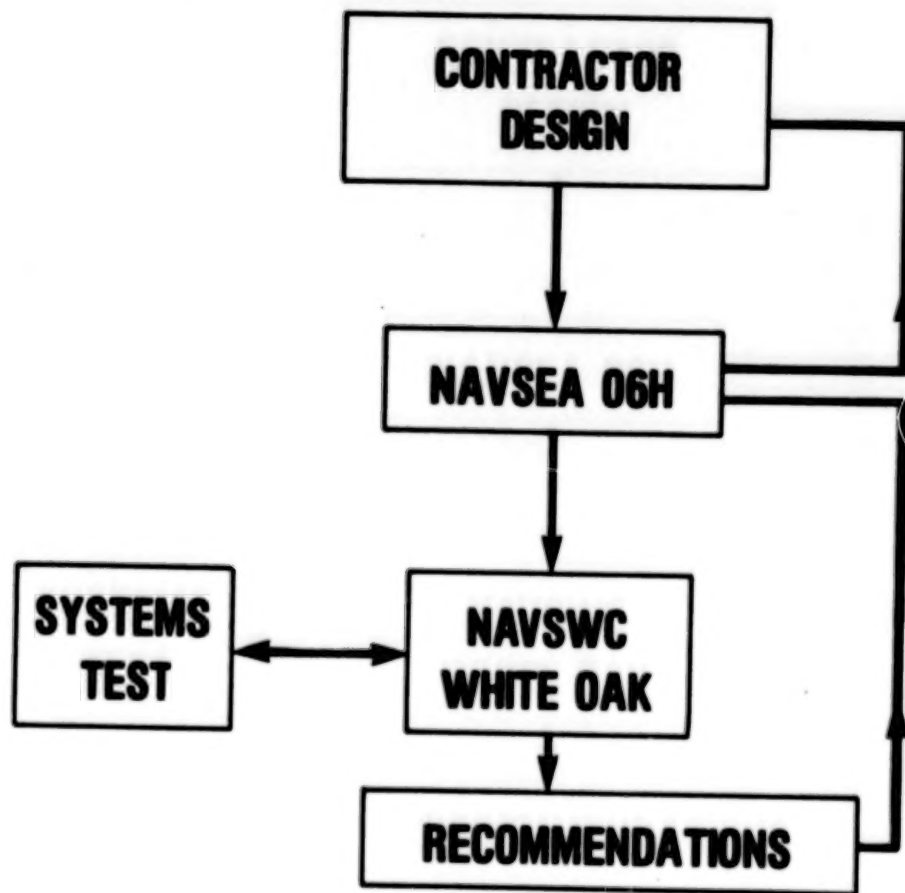


Figure 2

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PLACEMENT OF ELECTRICAL AND THERMAL FUSES IN TYPICAL CIRCUITS

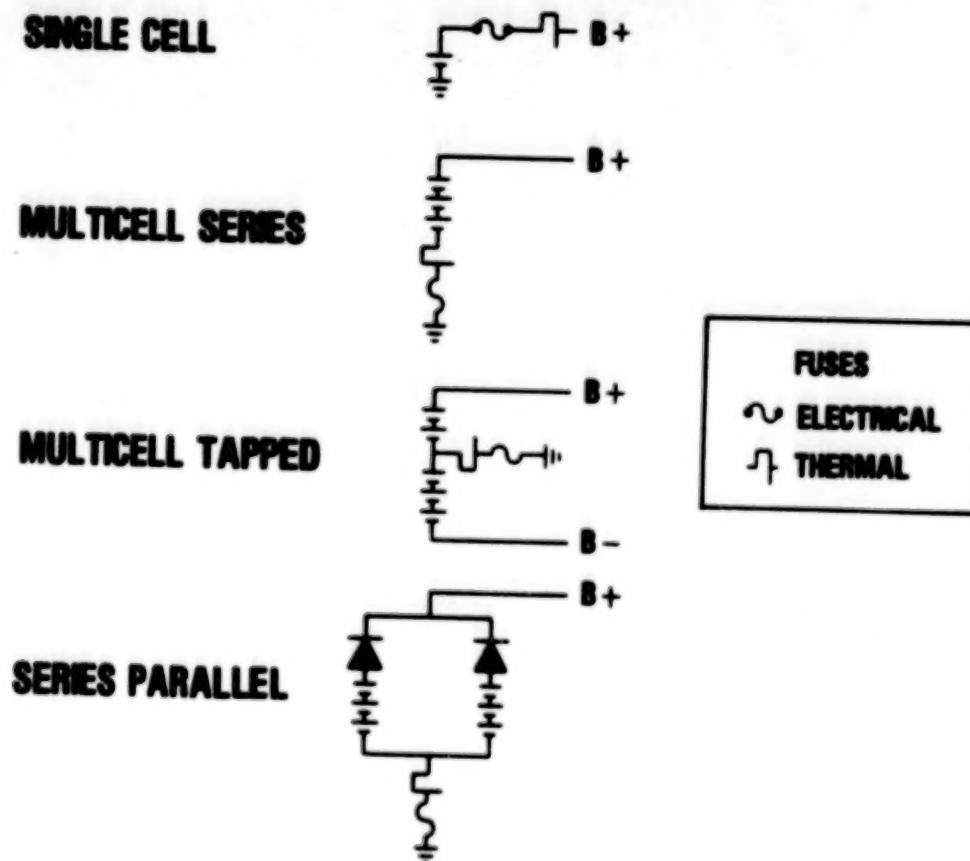


Figure 3

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PRIMARY LITHIUM BATTERIES,
SOME CONSUMER CONSIDERATIONS.

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ABSTRACT

Miniature lithium cells have become a commercial reality. Is there also a consumer market for the larger sizes of lithium batteries?

In an attempt to answer this question, the performance of several D size lithium batteries is compared with that of an equivalent alkaline manganese battery, and the relative costs of the different systems are compared.

It is concluded that opportunities exist in the consumer market for the larger sizes of the low rate and moderate rate lithium batteries, and that the high rate lithium batteries need further improvements before they can be recommended for consumer applications.

INTRODUCTION

Primary lithium batteries for ambient temperature applications have become a reality since the late 1960's. A great variety of lithium couples have been studied and more are under investigation. Despite the many lithium systems that may lead to useful products, as yet, only a limited number has reached the commercial product stage. Among the latter, the solid state lithium/iodine system is noteworthy as the first system to gain wide acceptance; it has almost completely displaced the alkaline zinc/mercuric oxide system from the pacemaker market. Some systems have reached a sufficiently advanced stage of development for finished products to be available in either sampling or production quantities. A representative selection of these includes: lithium/silver chromate, lithium/sulfur dioxide, lithium/carbon monofluoride, lithium/manganese diox-

ide, lithium/cupric oxide, and lithium/thionyl chloride. Other lithium systems are likely to be developed in the future as the lithium technology advances and as the markets for lithium batteries expand. Although the technology has become firmly established, the extent to which what lithium system will penetrate what consumer market remains an open question.

The success of the lithium systems is attributable to several factors. Foremost is their high energy density. This is particularly important for medical implant applications and for their use in portable devices. Secondly, the lithium systems have a long shelf life, and some of them perform much better than do conventional batteries over a wide temperature range, including low temperatures. Also, many of the lithium batteries have a good voltage regulation, which is desirable for most electronic applications.

In approaching the question of the future penetration of various markets, it may be useful to distinguish between:

- a. the governmental markets
- b. the industrial and OEM markets
- c. the consumer markets

The first two markets tend to be rational markets in the sense that specific performance requirements are stipulated for the various applications, and the sale/purchase negotiations and agreements contain readily recognisable objective components as elements of the decision-making process. These two markets will be excluded from consideration in this paper. Our concern is with the consumer market and some possible appraisals of lithium batteries by the consumer.

The consumer markets center on applications for which the purchaser as a private individual buys for his own purposes one or more batteries at the retail level. Occasional overlaps exist between the OEM and the consumer markets so defined. For example, if a camera manufacturer specifies a particular battery for his product and supplies the camera with the battery in place, there is a built-in, follow-on consumer replacement market that complements the OEM market for this battery product.

The purchasing decision of a consumer is influenced by many factors, not necessarily all rational. They include advertising, product appearance, store display, pricing, location of retail outlet, product performance, and other factors. In view of all these influences, the only reliable method of assessing the consumer response is to test market the product in question.

In the case of the larger sizes of lithium batteries, no such analyses are available to the public. We have to make some assumptions, therefore, in order to assess the probable response of the consumer to lithium batteries. The simplest approach, which is adopted here, is to assume that the consumer makes a rational purchasing decision based on price and performance. This avoids the highly problematic discussion of all the intangible factors that do in fact affect the consumer. At best, our discussion can be only an approximation to the actual consumer response.

The consumer market for lithium batteries is of interest to the battery manufacturers. It is also of interest to the Government since it is more economical for government agencies to buy commercially available batteries than to establish, at high cost, special purpose manufacturing facilities for the products needed by the Government.

BATTERY PERFORMANCE AND COST

Rather than considering all the lithium systems that have been studied to date, this discussion will focus on five of the most highly developed systems and on the alkaline manganese system for reference purposes. These systems are: Li/SO_2 , Li/SOCl_2 , Li/MnO_2 , $\text{Li}/(\text{CF})_n$, Li/CuO , and Zn/MnO_2 . In regard to the available cell sizes and their applications, they range from the small button and wafer cells for e.g. watches and calculators, through the medium size cells and batteries used in cameras and pagers, to the larger cylindrical sizes commonly employed in radios, flashlights, recorders, etc. The latter size, the D size cells (IEC designation R 20), will provide the basis for our assessment. Where actual data were not available, the performance of smaller cells was scaled to that of D size cells using the cell volume as a scaling parameter. Similar comparisons can be made for any cell size. It may be noted that the smaller the cell, the more the inactive cell materials control cell performance. Therefore, any differences observed in the performance of the larger D cells tend to reflect intrinsic system characteristics, which are of principal interest. Furthermore, the larger cell sizes are of particular interest since they relate to some large volume consumer applications of primary batteries.

DISCHARGE COMPARISONS

Discharge curves of the various systems are shown in

Figures 1A and 1B for room temperature discharges at average currents of 250 mA and 100 mA, respectively. The curves were obtained by interpolation or extrapolation of data available in literature published by the various manufacturers. Several features may be noted:

- a. the high rate Li/SOCl₂ HR system has a greater load voltage than any other lithium system, and it gives the longest service, except for the low voltage Li/CuO system.
- b. the low rate bobbin type Li/SOCl₂ LR cell gives a performance far inferior to that of the spirally wound Li/SOCl₂ cell at the higher rates of discharge, but its performance approaches that of the high rate cell at low rates of discharge.
- c. the performance of the solid depolariser lithium systems clusters together both in terms of load voltage and hours of service, except for the low voltage Li/CuO system.
- d. the Li/CuO system operates close to the voltage of the alkaline Zn/MnO₂ system, and it gives by far the longest service of any of the systems considered.

SOME ENERGY DENSITIES

The high energy density of the lithium systems is generally accentuated. For space and military applications, a high gravimetric energy density is important. For consumer applications, however, the volumetric energy density tends to be of greater interest. Figure 2 shows the relative volumetric energy densities of the various systems based on a 3 Volt D size battery operating to a 2 Volt cut-off. For the Zn/MnO₂ and Li/CuO systems, two ½D cells were configured in series. This equal volume, equal voltage comparison is the significant one from the consumer's point of view. It may be seen that the high rate Li/SOCl₂ system outperforms all the other lithium systems on an energy density basis, and that the latter give comparable performances among themselves and deliver more than twice the energy density of the alkaline Zn/MnO₂ system. On an energy density basis alone, the high rate Li/SOCl₂ system is certainly outstanding.

COST COMPARISONS

The price paid by the consumer for a given service tends

to control his response in the long term, and since price tends to be proportional to cost, an examination of battery costs is of interest. As noted, for some applications the consumer buys hours of service, i.e., coulombic capacity, and for others he buys energy. Furthermore, for each particular application, the consumer buys a battery to fit a pre-existing battery compartment in his battery operated device. Cost comparisons should be made, therefore, between cells of the different systems packaged into the same battery size and connected to operate over the same voltage range. It may be noted in this context that a high voltage system is wasteful of energy unless the user device takes advantage of that high voltage. Some cost comparisons are presented in Figures 3 and 4. In preparing the cost estimates, it was assumed that each of the batteries would be available from highly mechanised, high volume production lines. Under such circumstances, the cost of a battery is primarily a materials cost. Quotations were obtained from vendors of the materials needed to fabricate the various batteries, including the inactive materials, and the costs are current as of October, 1982. There is some latitude in the cost to the battery manufacturer of any particular material or component. For example, if he buys the battery case from a vendor, the cost is greater than if he manufactures the case himself. In order to maintain consistency between the costs shown in Figures 3 and 4, the costs were calculated on the assumption that all the required materials and components were purchased by the battery manufacturer. Thus, attention should be focussed on the relative costs of the various systems rather than on the absolute values themselves.

It may be seen that the alkaline Zn/MnO_2 system provides the lowest cost service in terms of cost per ampere-hours of service, and the Li/SOCl_2 system delivers the most expensive service; about 80% more expensive. The other lithium systems fall between these limits. Among the solid depolariser systems, the $\text{Li}/(\text{CF})_n$ system appears to be the most cost effective, costing only about 40% more than the alkaline Zn/MnO_2 system. However, this result must be tempered by the realisation that there is a considerable uncertainty in regard to the cost of $(\text{CF})_n$ in volume production.

If the high voltage of the lithium systems is fully utilised in a device, the relevant cost comparison is the cost per unit of delivered energy, Figure 4. Interestingly, the energy cost of the considered systems fall within a narrow range, about 5¢/Wh. Therefore, the cost of the energy delivered by any of the several lithium systems differs little from that of the alkaline Zn/MnO_2 system, and the cost per unit energy is not a distinguishing selection criterion per se.

CONJECTURED MARKET RESPONSE

Allowing the assumption that the consumer will make an objective purchasing decision based on cost and performance, what may be the implications of the preceding system characteristics? Before considering this question, the matter of battery safety needs to be raised. Information presented at this and earlier NASA Symposia suggests that high rate, soluble depolariser lithium batteries may be unsafe. Under certain circumstances they may explode with possibly adverse consequences for the user, including the potential inhalation of toxic fumes originating from the cells. In view of these known effects, the sale of high rate Li/SO_2 and Li/SOCl_2 batteries in the consumer market is highly problematic. Peters' analysis (Ref. 1) of exploding lead-acid batteries provides an interesting legal view of the matter of battery safety. An advertisement aimed at product liability attorneys by Patent Research Associates, Inc. (Ref. 2) reflects a similar concern. It states: "... Our staff of attorney-engineers specialize in searching the records of the U. S. Patent Office to obtain patents which show that your defendant had actual/constructive knowledge of the devices/methods which would have prevented your client's injury. ..." Until the high rate, soluble depolariser cells/batteries can be rendered safer than they are now, they need not be considered for consumer applications involving the larger cell sizes of interest in this paper. The low rate, bobbin type Li/SOCl_2 cells would probably be acceptable for many consumer applications when handled according to the manufacturer's directions. No low rate Li/SO_2 cell design has been developed to date, so the Li/SO_2 system can be excluded from consideration for the general consumer market. This leaves the solid depolariser systems and the low rate Li/SOCl_2 system as potential candidates for consumer applications.

In the low voltage range, the Li/CuO system is the only one considered in this paper. Note, however, that several other low voltage lithium systems are in various stages of development that may be considered for consumer applications. Since Li/CuO has the highest specific capacity among the low voltage lithium systems, the conclusions reached for this system would probably apply to the other low voltage systems as well when they are compared with the alkaline Zn/MnO_2 system. Furthermore, the cost of the other low voltage systems is not much less than that of the Li/CuO system.

The Li/CuO system provides about three times the service life of the alkaline Zn/MnO_2 system and would for that reason have considerable consumer appeal. Its cost is noticeably great-

er, however, which is a significant detractor in the consumer market. It is about 60% greater on an amperehour basis. From a manufacturer's point of view, the displacement of alkaline Zn/MnO_2 batteries by Li/CuO batteries would reduce the number of batteries sold to about one third, assuming a constant ampere-hour demand, while maintaining his dollar volume, but reducing his profit margins. Attempts to maintain his margins would lead to unacceptably high prices with a consequent decrease in demand. His incentives to effect the suggested replacement would be negative. In the case of miniature cells, which are not considered here, the relevant comparison is between Zn/HgO , $\text{Zn/Ag}_2\text{O}$, and lithium systems. For these cells, the lithium systems enjoy advantages that are evident from the penetration they have made already in various applications. Any success of the larger size Li/CuO cells in the consumer market would appear to depend upon successful promotions overcoming the cost disadvantages of this system. The same conclusion would apply to the other low voltage lithium systems.

A different situation prevails in the high voltage range where we may consider batteries operating at three volts or at multiples of three volts. In this case, the relevant comparison is between the unit energy costs of the various systems, Figure 4. It was noted that the various systems were essentially equivalent on this basis. Thus, a selection between the lithium systems and the alkaline system must be made with reference to some other characteristic. Consider the voltage of the systems. Referring to Figure 1B, it may be seen that Li/(CF)_n and Li/SOCl_2 LR both have a good voltage regulation, but they operate at different load voltages. This has some interesting implications. On a resistive load the lower voltage Li/(CF)_n system will deliver a lower current than the other system, but still within an acceptable range. It will, therefore, provide a somewhat longer service than indicated in Figure 1B relative to the higher voltage systems. This feature may be exploited in multi-volt batteries operating devices that accept a wide-range voltage input, for example, the 9 Volt transistor radio battery (IEC designation: 6F22) used with radios that can operate with inputs down to about 4.5 Volts. The alkaline version of this battery requires six alkaline Zn/MnO_2 cells in series and it delivers about 0.5 Ah of service. If the Zn/MnO_2 cells were replaced by lithium batteries, two lithium cells in series, e.g. Li/(CF)_n , Li/MnO_2 , or Li/SOCl_2 LR cells, would deliver about twice the capacity of the equivalent alkaline Zn/MnO_2 battery and still operate within an acceptable voltage range for the radio. Among these systems, the Li/SOCl_2 LR system would give the better transistor radio volume control because of its higher voltage, and the lower voltage Li/(CF)_n system would give the longer service, but poorer volume control because of its lower operating voltage. The Li/MnO_2 system, on the other hand,

would be intermediate between the two, having a good volume control capability during the first half of its discharge and a longer life towards the end of its discharge. On a voltage selection basis, therefore, the replacement of three alkaline cells by one lithium cell would present cost advantages to the manufacturer and performance advantages to the consumer. It would appear that the 9 Volt transistor radio battery is a product where the interests of both manufacturer and consumer converge by the adoption of the lithium technology. Similar arguments apply to other high voltage batteries.

In regard to the larger size three volt, solid depolariser lithium batteries, C and D size, designed for high rates of discharge, there is still the question of product safety to be considered. They comprise an intimate mixture of strong oxidising agents in a finely divided state with a flammable organic solvent. Thermodynamically, this is an unstable system, and the greater the amounts of materials present in intimate contact, the greater the inherent risk of a conflagration. Little has been published on the hazard potentials of such cells, and until the requisite information is available, the entry of these products into the consumer market should be viewed with some concern.

CONCLUSIONS

The present situation may be summarised briefly. The miniature lithium cells have already demonstrated their usefulness and success in the OEM and consumer markets. The performance and cost comparisons indicate that the medium size lithium systems are superior in performance to alkaline cells, that superiority, however, is associated with a commensurate increase in cost, and it is not immediately obvious that the lithium batteries will displace alkaline batteries on a broad basis in the consumer market. Applications do exist, however, where performance is at a premium and where the lithium batteries would be preferred, but it is not certain that the volume of such premium applications would warrant the establishment of the required production facilities. A limited number of high volume applications do exist, nevertheless, where advantages accrue to both the consumer and the manufacturer by the use of medium size lithium batteries, the 9 Volt transistor radio battery being a good example. It would appear that several lithium systems can compete on nearly equal terms for such applications. The general acceptance in the consumer market of the larger size, high rate, soluble depolariser and high voltage, solid depolariser lithium batteries remains problematic on the grounds of safety, and it is not yet clear that this situation will change in the near future.

REFERENCES

1. Peters, George A.: Battery Explosions - With Acid Ejected Into Eyes and Face. Part I. Trial, June 1982, pp. 64-69, and 86.

Peters, George A.: Battery Explosions - Cause and Cure.
Part II. Trial, July 1982, pp. 100-105.

2. Advertisement, Trial, July 1982, p. 104.

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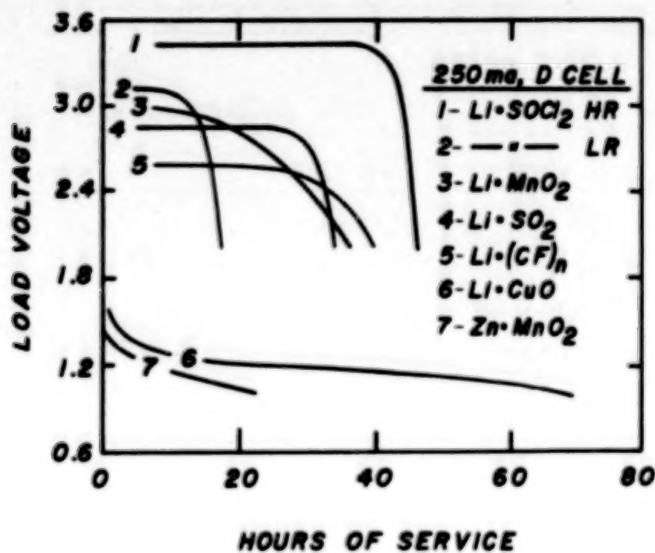


Figure 1A

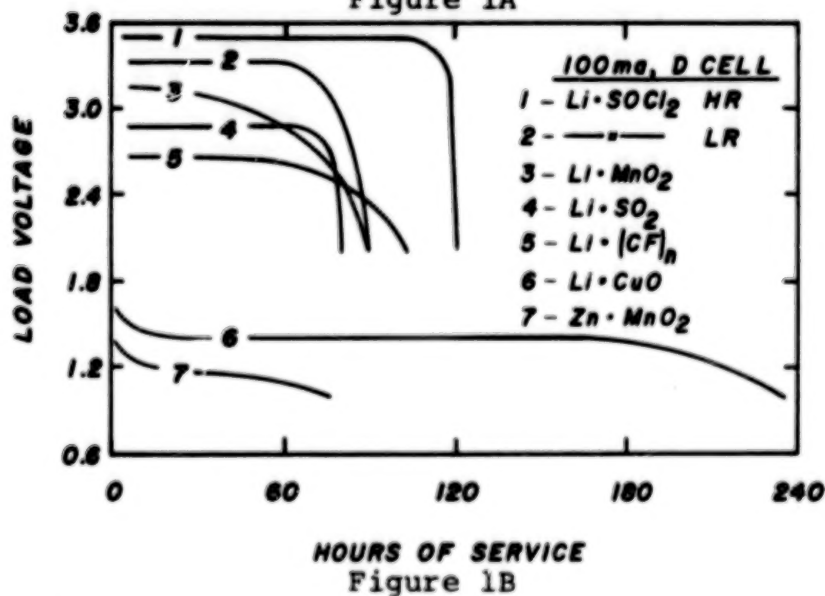


Figure 1B

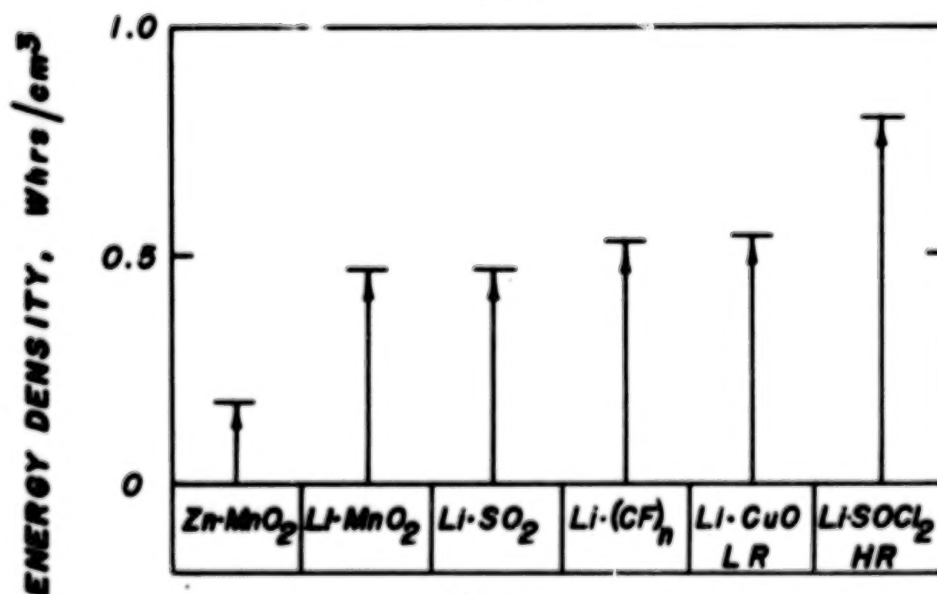


Figure 2

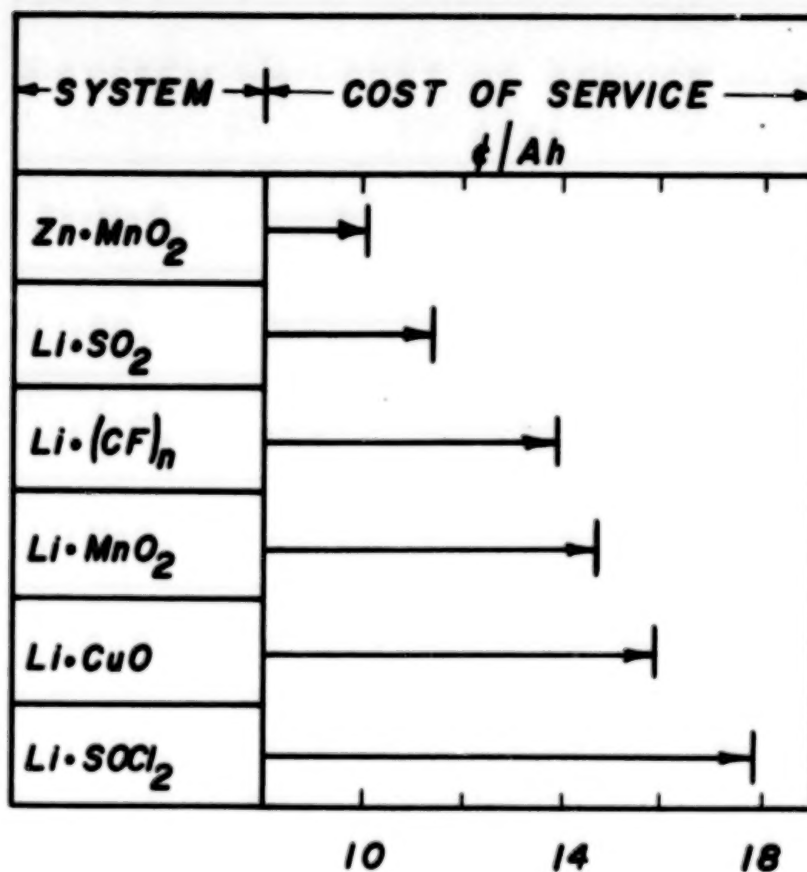


Figure 3

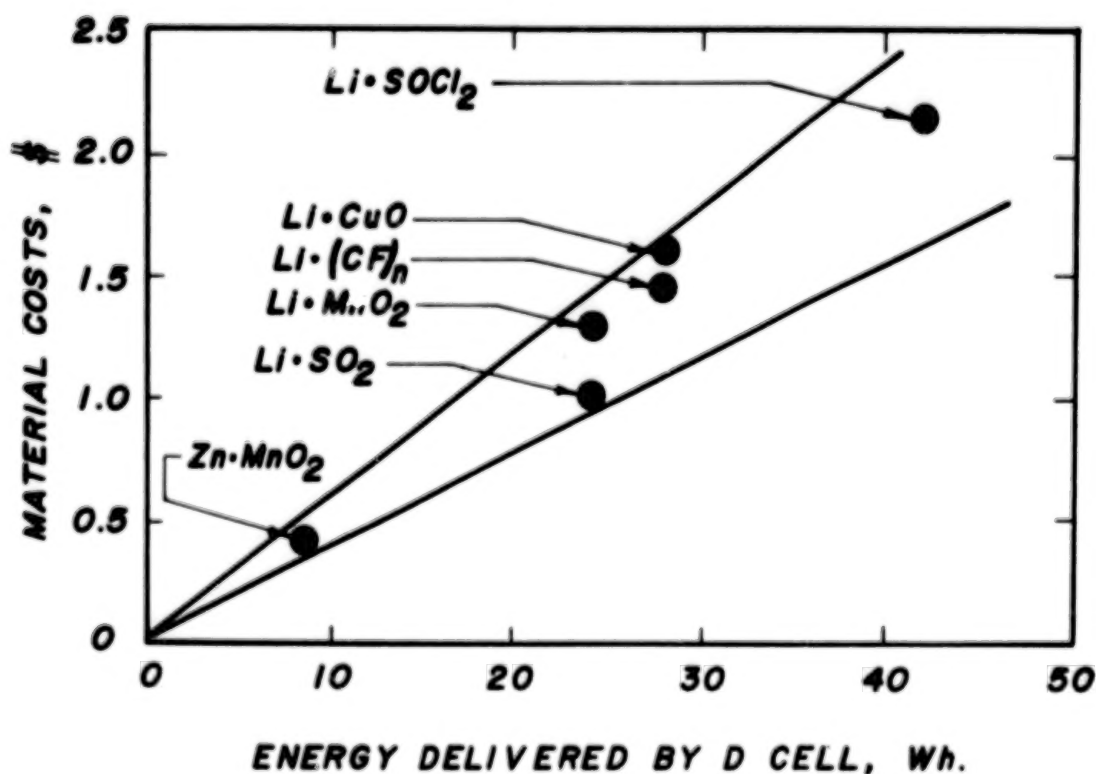


Figure 4

OTHER PRESENTATIONS

FORCED OVERDISCHARGE RELATED SAFETY ASPECTS

K.M. Abraham, E.I.C. Laboratories

SAFETY TESTS

P. Krehl, Electro Chem Industries

LOW TEMPERATURE PERFORMANCE TESTS

F. Goebel, General Telephone Electronics

Li/SOCL₂ Cell: ANODE/CATHODE LIMITED DESIGNS

M. Domeniconi, Altus Corp.

DESIGN OF A SAFE CYLINDRICAL LITHIUM/THIONYL CHLORIDE CELL

D. Johnson, Union Carbide Corporation

VALIDATING CELL/BATTERY SAFETY

D. Chua, Honeywell

FORCED OVERDISCHARGE RELATED SAFETY ASPECTS
OF Li/SO_2 AND Li/SOCl_2 CELLS

BY

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NOVEMBER, 1982

LI/SO₂ CELLS: CIRCUMSTANCES OF SAFETY CONCERNS

- (I) FORCED OVERDISCHARGE OF LI/SO₂ CELLS. THIS SITUATION, EXPERIENCED BY A WEAK CELL IN A SERIES-CONNECTED BATTERY, HAS BEEN THE MOST FREQUENT CAUSE OF CELL OR BATTERY VENTING OR EXPLOSION.

- (II) INCREASED VULNERABILITY OF PARTIALLY DISCHARGED AND STORED LI/SO₂ CELLS AND BATTERIES TO SUBSEQUENT ABUSE; E.G., SHORTS, HIGH CURRENT PULSES, OVERDISCHARGE OR INCINERATION. THIS IS A PARTICULARLY HAZARDOUS CONDITION IN PRACTICAL SITUATIONS.

- (III) LOW TEMPERATURE DISCHARGE, PARTICULARLY WHEN A CELL IS DRIVEN INTO VOLTAGE REVERSAL AND SUBSEQUENTLY WARMED UP TO ROOM TEMPERATURE.

M. W. RUPICH AND K. M. ABRAHAM, FIRST QUARTERLY REPORT, NSWC CONTRACT NO. N60921-81-C-0084, MAY 1981.

EXPERIMENTAL RESULTS WITH TWO TYPES OF
C-SIZE COMMERCIAL Li/SO_2 CELLS

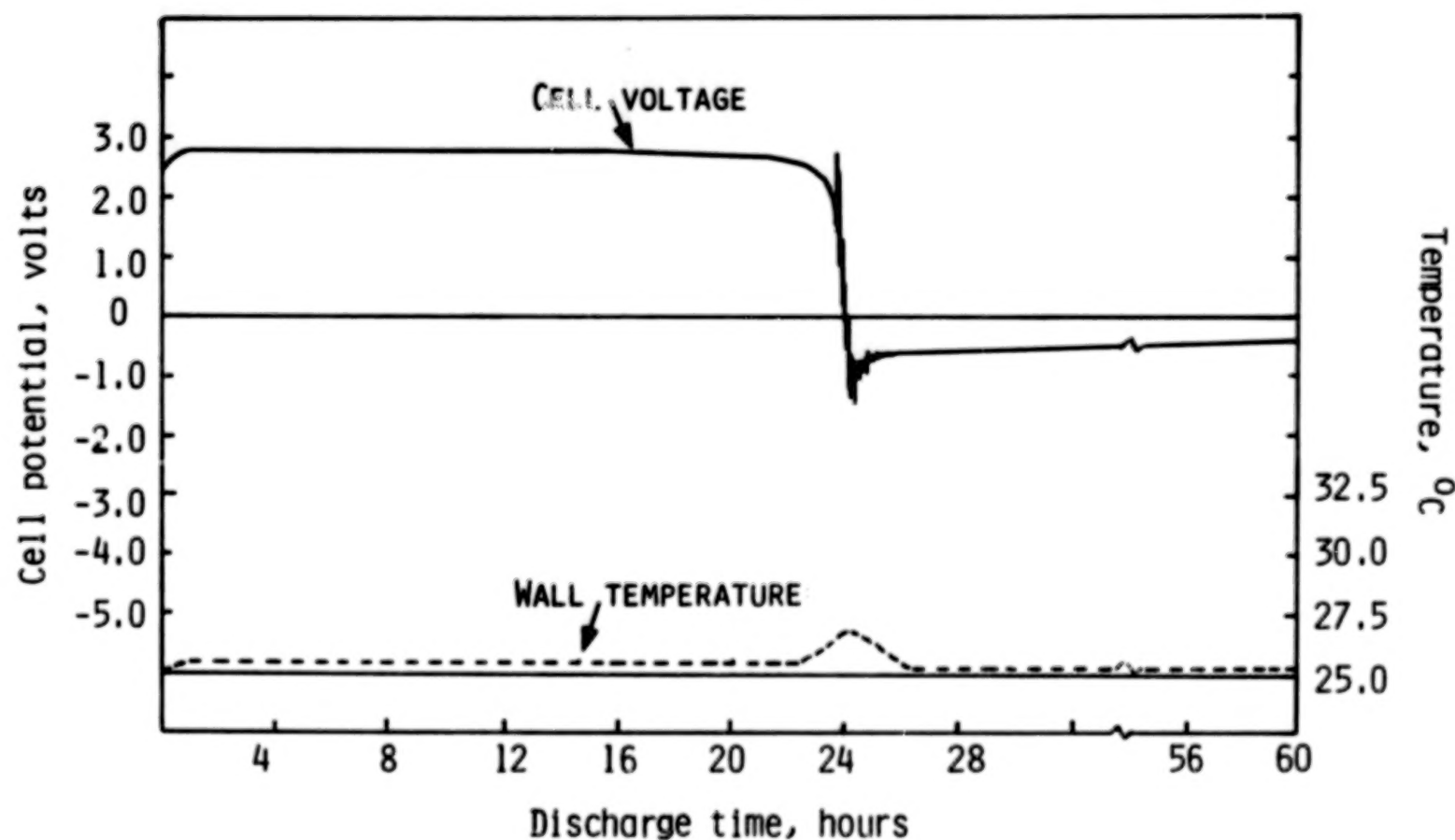
K. M. ABRAHAM, M. W. RUPICH AND L. PITTS
FINAL REPORT, NSWC CONTRACT No. N60921-81-C-0084
REPORT No. NSWC TR 82-148, APRIL 1982

MAJOR CHARACTERISTICS OF THE TWO COMMERCIAL C-SIZE CELLS*

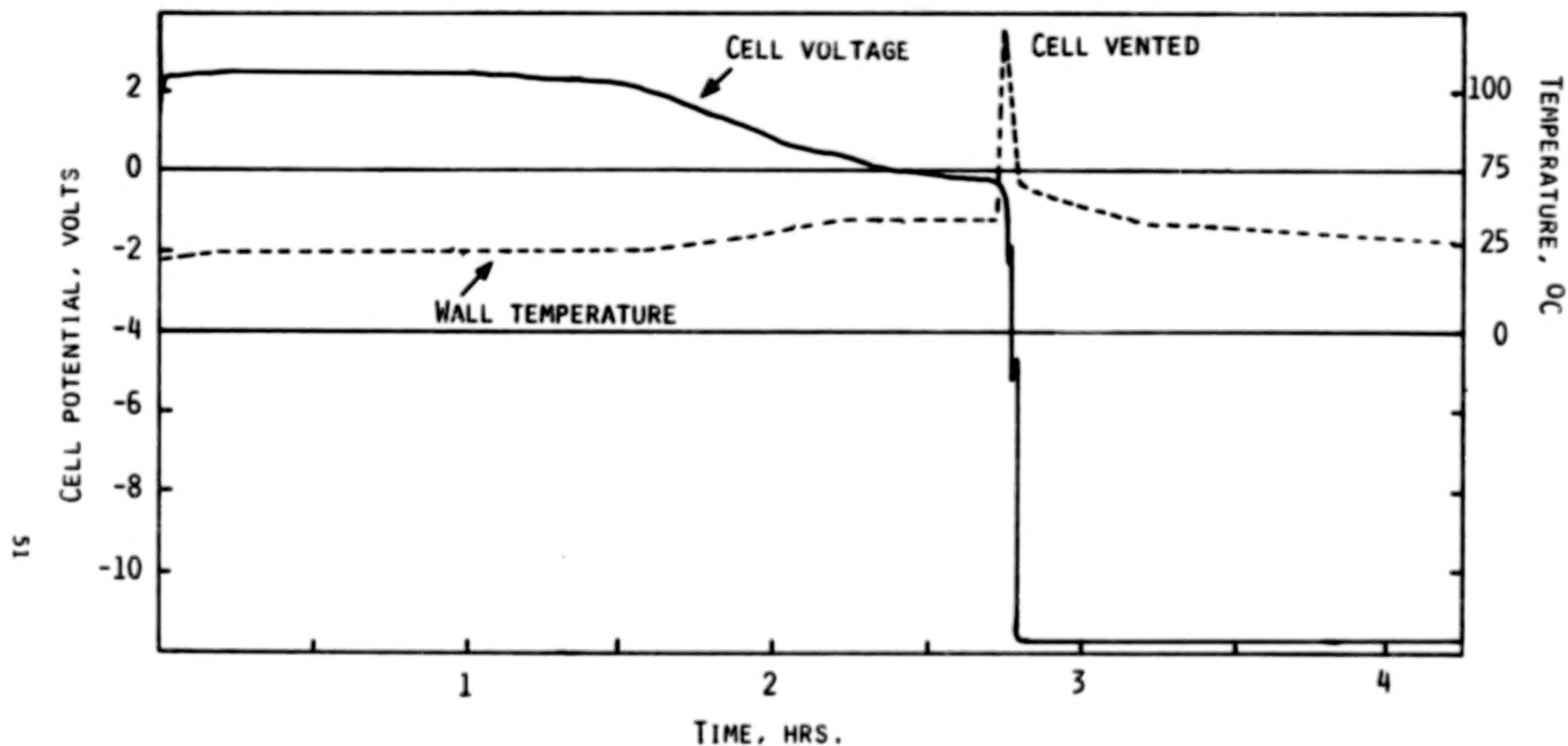
<u>CELL TYPE</u>	LITHIUM	SO_2	Li/SO_2	AREA OF CARBON
	<u>A-HR</u>	<u>A-HR</u>	<u>RATIO</u>	<u>CATHODE</u> <u>(BOTH SIDES), cm^2</u>
TYPE A	~ 6.7	~ 3.7	1.81	125
TYPE B	~ 4.8	~ 4.0	1.20	175

*BASED ON OUR ANALYSIS.

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DISCHARGE AND FORCED OVERDISCHARGE OF A TYPE A CELL AT 25°C. CURRENT, 150 MA: CAPACITY REALIZED TO 0.0 VOLT, 3.5 AH. CELL EXHIBITED NO HAZARD DURING 36 HOURS OF OVERDISCHARGE. POST-MORTEM ANALYSIS SHOWED: CH₄ IN THE GAS PHASE; DI- AND TRI-ACETONITRILES ON THE ANODE ALONG WITH Li₂SO₃ AND Li₂S₂O₄; NO ORGANIC PRODUCTS ON CATHODE.



DISCHARGE AND FORCED OVERDISCHARGE OF A TYPE A CELL AT 1 AMPERE AT 25°C. CELL CAPACITY REALIZED TO 0.0 VOLT, 2.35 A-HR. CELL VENTED AFTER 0.34 HR INTO OVERDISCHARGE. GASES RELEASED FROM THE CELL INCLUDED THE HAZARDOUS MATERIALS, CS₂, COS, CO₂, H₂S, CH₄, C₂H₄, C₂H₂.

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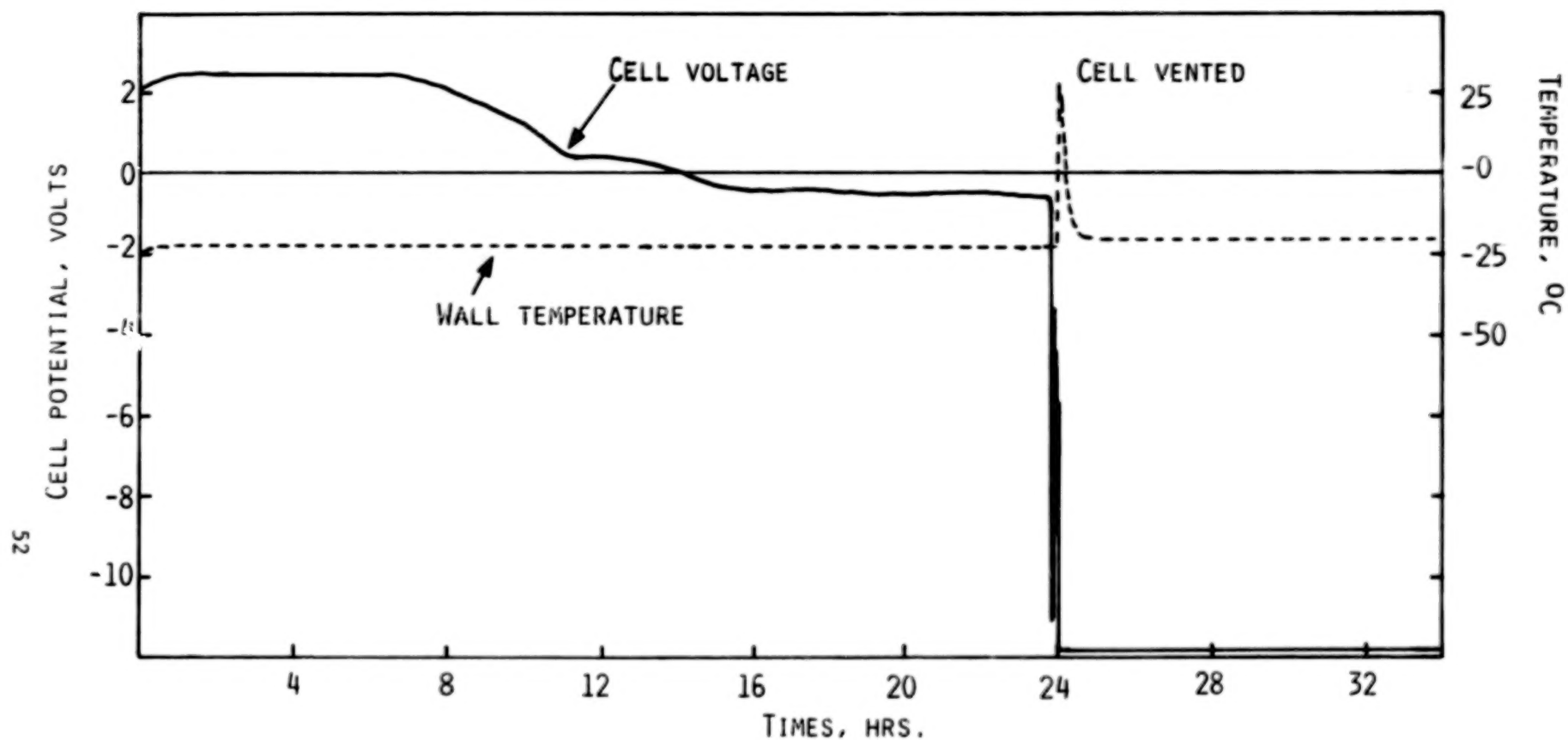
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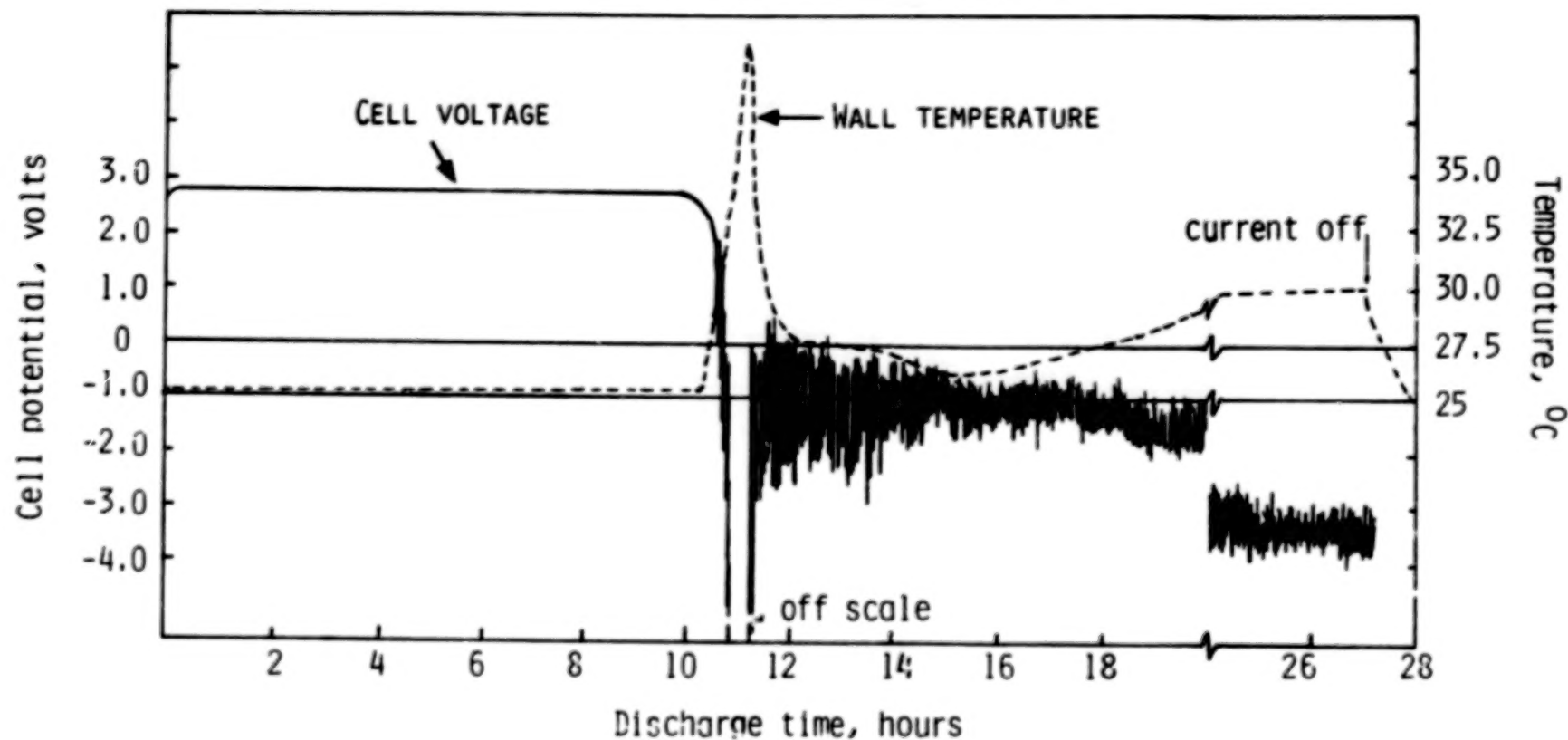
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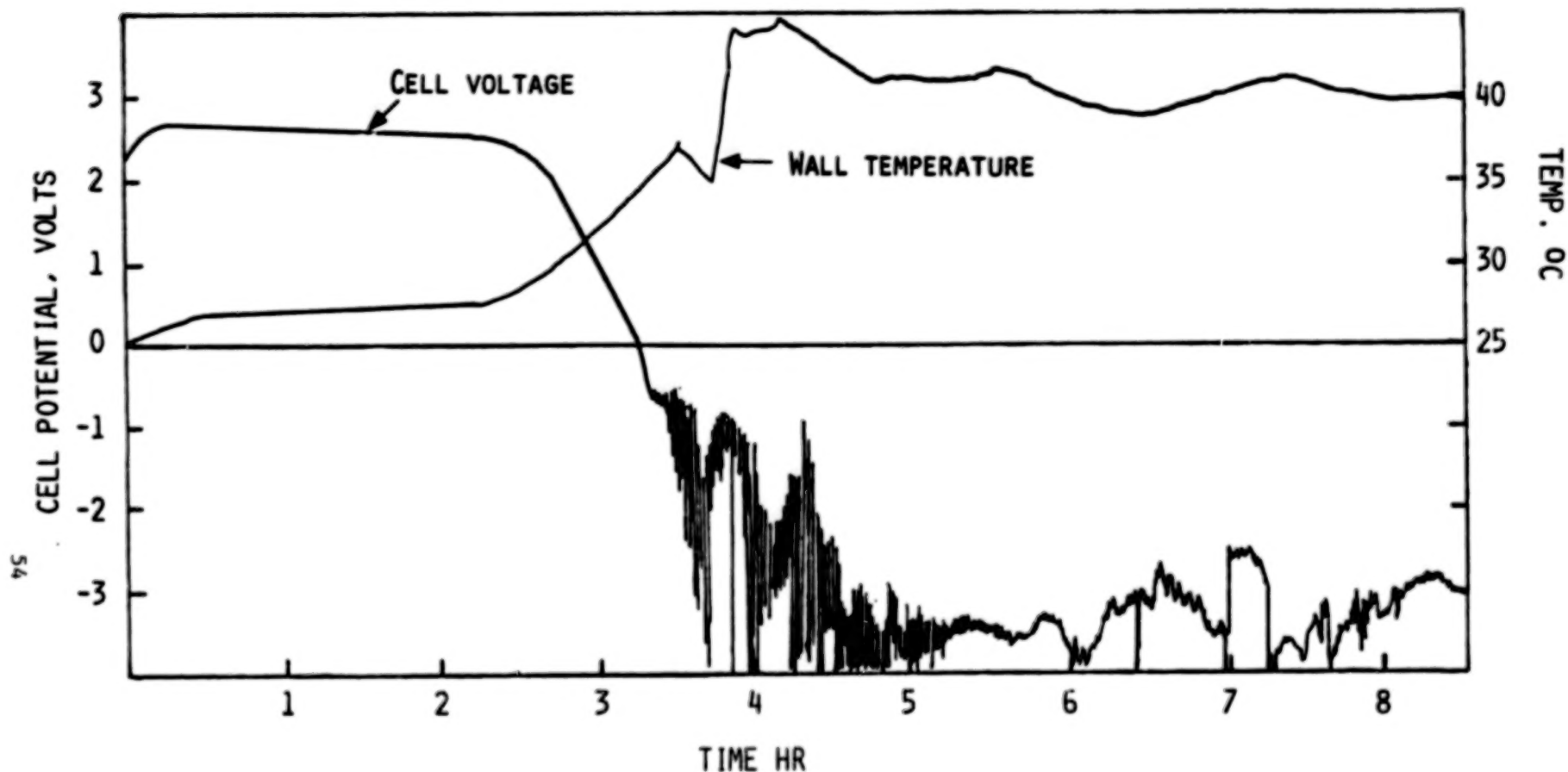
DISCHARGE AND FORCED OVERDISCHARGE OF A TYPE A CELL AT -25°C AT A CURRENT OF 150 MA. CAPACITY REALIZED TO 0.0 VOLT, 2.1 AH. CELL VENTED WITH FLAME AFTER ~ 10 HRS INTO OVERDISCHARGE. GASES RELEASED INCLUDED THE HAZARDOUS MATERIALS, CS_2 , COS , CO_2 , H_2S , CH_4 , C_2H_4 , C_2H_2 .



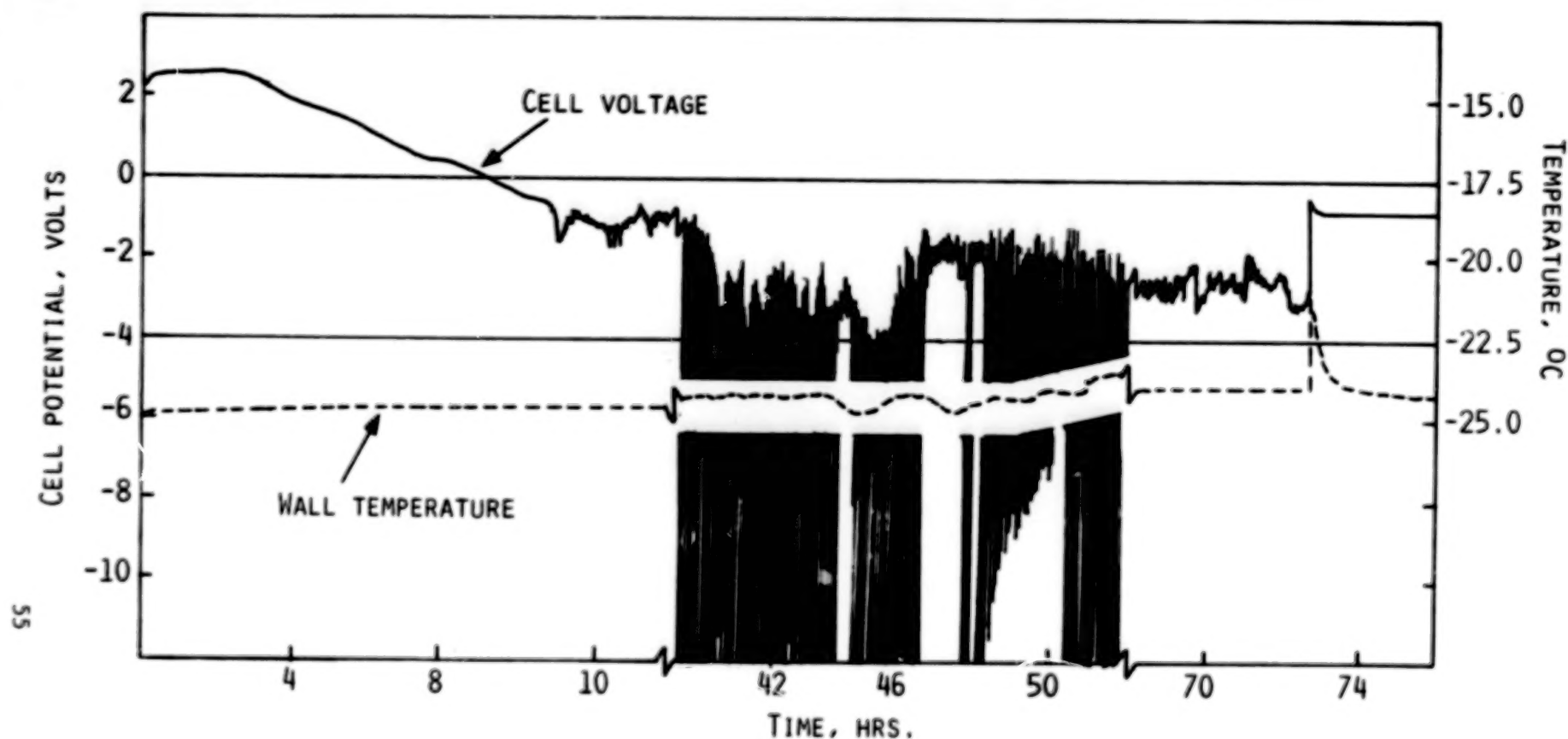
DISCHARGE AND FORCED OVERDISCHARGE OF A TYPE B CELL WITH 300 MA AT 25°C. CAPACITY REALIZED TO 0.0 VOLT, 3.2 AH. CELL EXHIBITED NO HAZARD DURING 17 HOURS OF OVERDISCHARGE. POST-MORTEM ANALYSIS SHOWED IDENTICAL PRODUCTS AT THE SAME LOCATIONS AS IN TYPE A CELLS!

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DISCHARGE AND FORCED OVERDISCHARGE OF A TYPE B CELL WITH 1 AMPERE AT 25°C. CAPACITY REALIZED TO 0.0 VOLT, 3.24 AH. CELL EXHIBITED NO HAZARDS DURING 7.5 HOURS OVERDISCHARGE. POST-MORTEM ANALYSIS SHOWED SAME REACTION PRODUCTS AS IN CELLS DISCHARGED AT THE LOWER CURRENTS.



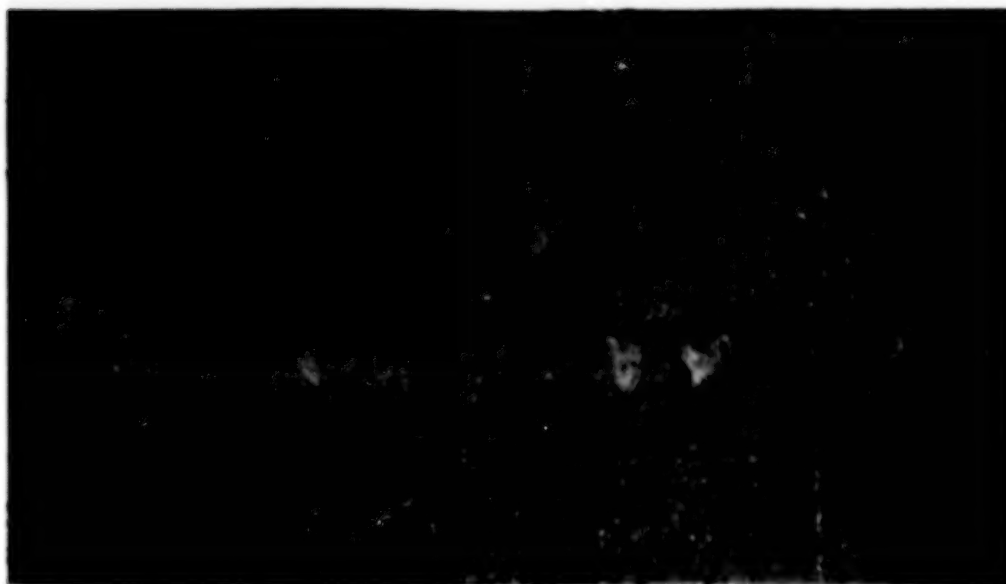
DISCHARGE AND FORCED OVERDISCHARGE OF A TYPE B CELL AT -25°C WITH A CURRENT OF 300 MA. CAPACITY REALIZED TO 0.0 VOLT, 2.7 AH. FORCED OVERDISCHARGED FOR ~ 64 HOURS. AFTER ~ 3 HOURS OF OVERDISCHARGE CELL VOLTAGE BEGAN TO SHOW LARGE FLUCTUATIONS. CELL DID NOT VENT BUT POST-MORTEM ANALYSIS SHOWED GASEOUS PRODUCTS: CH_4 , COS , CS_2 , H_2S AND CO_2 . NO C_2H_2 OR C_2H_4 AS IN VENTED CELLS FOUND. SEPARATOR SHOWED BURNED AREAS (SEE NEXT SLIDE). CATHODE BURNED WHEN SCRAPPED! THE CATHODE FROM ANOTHER, SIMILARLY TESTED, CELL BURNED VIOLENTLY WHEN PULLED OUT!!

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SEPARATOR BURNED



SEPARATOR BURNED

PHOTOGRAPH SHOWING THE BURNED AREAS OF THE SEPARATOR FROM A TYPE B CELL AFTER A FORCED OVERDISCHARGE AT -25°C (SEE PREVIOUS SLIDE). NOTE THAT THE CATHODE INDICATED POTENTIAL SHOCK SENSITIVITY. THESE BURNED AREAS AND THE GASEOUS PRODUCTS INDICATED THAT LOCALIZED HAZARDOUS REACTIONS HAD OCCURRED DURING FORCED OVERDISCHARGE.

OVERVIEW OF LI/SO₂ CELL SAFETY

- FORCED OVERDISCHARGES OF THE LI/LIBR, CH₃CN/SO₂ CELL CAN RESULT IN UNSAFE BEHAVIOR SUCH AS VENTING WITH FIRE AND RELEASE OF TOXIC GASES.

- THE HAZARDS MAY BE MINIMIZED OR ELIMINATED BY CAREFUL CELL DESIGN CONSIDERATIONS AND PRACTICE OF HIGH STANDARDS OF QUALITY CONTROL IN CELL MANUFACTURE.

- SEEMINGLY SAFE CELLS AT 25°C (TYPE B) WHEN FORCED OVERDISCHARGED AT -25°C, EVEN AT LOW CURRENTS, EXHIBITED INCIP-
IENT SIGNS OF HAZARDS. THEIR CATHODES INDICATED SIGNS OF SHOCK
SENSITIVITY.

- THE APPARENT ABSENCE OF VENTING OR EXPLOSIONS IN LOW TEMPERATURE TESTS DOES NOT NECESSARILY INDICATE SAFE CELLS. WE RECOMMEND CELL TESTING AT -25°C FOLLOWED BY CAREFUL PRODUCT ANALYSIS BEFORE CERTIFYING CELLS FOR FIELD APPLICATIONS.

- THE REPORTED HAZARDS ASSOCIATED WITH PARTIALLY DIS-
CHARGED AND STORED CELLS REMAIN TO BE UNDERSTOOD. AGAIN, CAREFUL
CHEMICAL ANALYSIS APPEARS TO BE THE PROPER APPROACH.

FORCED OVERDISCHARGE BEHAVIOR OF Li/SOC12 CELLS

● WE INVESTIGATED THE FORCED OVERDISCHARGE BEHAVIOR OF SPECIALLY INSTRUMENTED C-SIZE Li/SOC12 CELLS CONSTRUCTED WITH SPIRALLY WOUND ELECTRODES. THE CELLS WERE CATHODE LIMITED, ANODE LIMITED OR LI LIMITED.

REFERENCES

- 1) K. M. ABRAHAM ET AL., PROC. 28TH POWER SOURCES SYMPOSIUM, ATLANTIC CITY, NJ, JUNE 1978.
- 2) K. M. ABRAHAM AND R. MANK, J. ELECTROCHEM. SOC., 127, 2091 (1980).
- 3) K. M. ABRAHAM AND R. MANK, PROC. 29TH POWER SOURCES SYMPOSIUM, ATLANTIC CITY, NJ, JUNE 1980.

WE FOUND THAT:

- CATHODE LIMITED Li/SOCl_2 CELLS WERE SAFE DURING FORCED OVERDISCHARGE FOR LONG PERIODS OF TIME.

- LITHIUM LIMITED Li/SOCl_2 CELLS IN WHICH PRACTICALLY ALL Li HAD BEEN USED UP BEFORE CELL REVERSAL DID NOT EXHIBIT HAZARDOUS BEHAVIOR. CAN THIS SITUATION BE CONSISTENTLY ACHIEVED IN PRACTICE WITH A CELL REQUIRED TO PERFORM OVER A WIDE RANGE OF CURRENT DENSITY AND TEMPERATURE?

- ANODE LIMITED Li/SOCl_2 CELLS, BUT NOT Li LIMITED, EXHIBITED DETONATIONS, ALL DURING OVERDISCHARGES AT RELATIVELY LOW CURRENT DENSITIES OF $\leq 1 \text{ mA/cm}^2$. ANODE POTENTIALS $> 4\text{V}$ WITH LARGE OSCILLATIONS PRECEDED THE EVENTS. THE EVENTS WERE CONFINED TO THE ANODE AND THE TEMPERATURE ROSE HIGH ENOUGH TO MELT Ni GRIDS!

- THE INITIATION PROCESSES OF THE HAZARDS ARE NOT KNOWN.

- WHILE CHLORIDE OXIDES MAY BE FORMED BY OXIDATION REACTIONS IN THE CELL, ALL CLAIMS TO DATE ARE WITHOUT SUFFICIENT EVIDENCE AND APPARENTLY CONTRARY TO THE KNOWN CHEMISTRY OF CHLORINE OXIDES (SEE M. M. ROCHKIND AND G. C. PIMENTAL, J. CHEM. PHYS., 42, 1361 (1965). M. SCHMEISSER AND K. BRANDEL IN ADVANCES IN INORGANIC AND RADIOCHEMISTRY, VOL. 5, H. J. EMELEUS, EDITOR, ACADEMIC PRESS, INC., NY, P. 41 (1963) .

- WE RECOMMEND FURTHER INVESTIGATION OF THE SAFETY RELATED CHEMISTRY OF Li/SOCl_2 CELLS, INCLUDING STUDIES OF THE FORCED OVERDISCHARGED, AND PARTIALLY DISCHARGED AND STORED CELLS.

SAFETY TESTS

by P. Krehl, Electro Chem Industries

Thank you. We are quite concerned with safety at Electro Chem Industries. About 50% of our time is spent on safety studies of focus systems and manufacturing. The cells have shown themselves to be quite abuse resistant to forced overdischarged conditions, charged sequences, and short circuits. However, during a qualification test that was performed at Johnson Space Center the cells have shown that under very specific conditions they may be less tolerant to a forced over discharge situation. As most of you know, a safety alert was issued and it described in general the conditions set forth which may cause cells to fail. We have initiated a test program at Electro Chem to test double A cells and D cells with respect to those conditions.

I would like to briefly show you these preliminary results on those forced overdischarge tests. The conditions that I used to test the double A and D cells were as follows: The cells were discharged under very efficient rates to either, 50% of delivered capacity or down to about 1.5 volts plus or minus 0.5 or down very close to 0 volts or approximately 0.2 volts. Next, the cells were allowed to stand on open circuit for a period of about three to four weeks and then the cells were forced over-discharge at a relatively higher rate. This is the sequence at NASA founded to show problems in the cells. The first slide is just a reference point. This is a D cell first overdischarged at one ampere, and it is typically how we do our safety tests, you will see that. It is a continuous test; there is no break, but the cell is forced into reversal. We have done many cells this way, uppers 50 to 100, and we have never found any problem with the cell. You see the only thing is that at the reversal point you will get a slight rise in temperature, of course applying to the point of which the cells goes into reversal. Then the voltage appears to slack up at about -0.2 volts and the temperature goes back down to room temperature.

This is a D cell first overdischarge at one ampere. It was previously discharged with 50% level, or approximately 7.5 ampere-hours were delivered under about 300 million drain rate. The cell was self set for two to three weeks on open circuit and it was forced at a constant current of one ampere, inter-volted reversal. You see, basically it gives the same characteristics as a fresh cell--maybe a little higher temperature rise and a reversal point, but the voltage and the temperature finally stabilize out.

The cell that was discharged down to the two volt level and then subsequently allowed to stand on open circuit and forced overdischarged on that is one ampere, as shown in this slide. We found no problems with cells taking down to this voltage

SAFETY TESTS

level in a D cell. There is a tendency for the cells to go into reversal, much deeper in this case, down to about -6 volts, or you get the same temperature rise at the reversal point that the cell and the temperature both equilibrate out. I should point out that when we do forced overdischarge tests in this manner, our power source is set at one ampere constant current. But we do limit the source voltage to about a 10 volt limit. We do not let it free flow to 40 or 50 volts. I think that there may be differences seen in tests if you have a higher power driving a cell than if it were, say, one driven by D cells may be at three or 4 string series.

This is a cell that was discharged down to about 0.2 volts and forced into voltage reversal after about three weeks stand on open circuit. You will see that again everything appears fine. Most of these cells that were tested this way showed no problems. There were, however, two cells out of the group that did show a higher temperature spark after about 15 hours or so into tests. Some actually showed a higher temperature spark at about 30 seconds after onset of testing. These sparks were running up as high as 100° to 200° centigrade. It depended upon the placement of the thermocouple as to what temperatures were read on the skin. However, I should point out that the glaucocoeia was never ruptured in any of these cases and the cell was always intact.

This is just an expanded--the first eight minutes of the last slide is to show that this may not be a true warrants, constant current for the full portion of the test because of the 10 ampere limit on the source voltage. You see, it takes approximately three minutes for the current to get up to the one ampere rise, or in other words; the cell that is discharged down to 0.2 volts has quite a high internal resistance and without that higher power level it just cannot, it will not, allow one ampere current to flow through it.

This is a comparison. In this cell we let the source voltage float to whatever this cell needed to drive the one ampere and the constant current source that we had was 30 ampere to 40 volt source. We had plenty of power and it takes only about 20 to 25 volts to allow constant current at one ampere. But again, there was not much difference in either cell driven with 10 or 20 volts behind them.

As I mentioned before, we did have a few cells that showed a high temperature spark and this is just a graph showing that. The temperature on these did go over scale. They are a little over 250° celsius, and approximately 30 second or so into onset of test. Just in summary of the D cells then, these are

SAFETY TESTS

the test sets we are performing. We did a constant current test and also we drove cells into reversal by putting cells in a series package of one test cell driven by three fresh double D cells. We found that there was not much difference from the results that we got. The numbers in the boxes are the number of cells tested at the particular voltage level and you will see that we can run into some problems if the cells are discharged efficiently down to 0 volts, allowed to stand on open circuit, and then driven into voltage reversal after about two to three weeks. About two out of nine are constant current, and another two cells were driven by buried packs.

Double A cells--I will just show this as a beginning reference point. These are tested in much the same manner. This is a forced overdischarged of a fresh double A at 200 milliamperes and again it shows about the same characteristics as the D cell does. The increase in temperature is at the voltage reversal point, and also after that the voltage and the temperature stabilize out.

Cells discharged down to 50% and then allowed to stand on open circuit followed by the forced overdischarge are shown in this graph. So it is typically once you start loading it, more negative voltage than a fresh cell. We did again experience some high temperature events around the 14-18 hour mark of the test. This is driven by D cells (three cells in a series), it would be about on 10 volt source and it was driven through a 122 ampere resistor which would equal out to about 100 milliamperes constant current. You see the current is not quite constant; the D's do force current at about 100 milliamperes, but as the cell goes into reversal, and has a little more resistance to it, the current may drop off to 80 milliamperes or so. But it is held fairly constant by the D cells.

These are double A cells driven again by D cells. These were discharged down to the one and one-half volt level; also stored on open circuit for about two to four weeks, and then forced overdischarged. The profile is about the same. The cell is going into voltage reversal and again at about 20 hours we can see a high temperature spark and also two cells out of the group actually vented through the side of the case. Now, it was not a violent vent. Actually, what happened was there was a small hole burned in the side of the case and it released gases, but there was no fragmentation of the cell. The gas and metal seal was intact and the cells basically just sat where they were on the test bench. But, again, the temperature recorded here on the skin could vary quite a bit depending on where we had the thermocouple. I should point out that the vents, where they burned through the side of the case,

SAFETY TESTS

typically--all of the time, were either on the top or the bottom of the cell. And the cell casing and the double A cell is a three or four stainless steel and it is about 12 mil. thick, compared to a 31 mil. on a D cell.

We also drove cells by putting them in series with double A cells instead of a series with D cells just to more closely simulate what would happen in a battery pack because you would not mix cell sizes. And we got about the same results although the ventings were less in number. And then finally I will show you the summation of the double A test. Again, there are two types of discharges driven by D cells, driven by A cells, and the three different voltage levels and you can see that in most cases we have no events occur until we got down to approximately one and one-half volts in discharge or less. We believe that the key factor here is that the cells are allowed to stand on open circuit for that period of time and there must be some changes going on there. We have not fully characterized that yet. We are doing more studies, and also as noted there, the venting does occur both at the top or the bottom of the case and not just randomly at any portion of the cell case. Maybe saying that there are specific reactions going on in the cell and not just generalized.

Thank you.

LOW TEMPERATURE PERFORMANCE TESTS

by F. Goebel, GTE

We are presently on a government contract to investigate cell performance at extremely low temperatures and to look at some materials which could be used to make a cell completely electrochemically inert for the purpose of deactivation. [Figure 1] Shows the behavior of standard electrolyte (we call it 1.8 salt concentration) on cooling down to -180 degrees with liquid nitrogen and on warming back up to room temperature. You see on this cooling and warming curve basically two small plateaus where some heat is generated within the test tube and it indicates that between 50-60 degrees something happens. We assume the electrolyte is freezing out. These two plateaus are basically on the same level. I have heard discussions before that determining the freezing point of electrolyte is not that simple. I do not want you to take this result that serious-- that the freezing point is exactly at -55 to 60 degrees centigrade. For some of the future results it might be important to keep this in mind though.

A double A cell with the same electrolyte concentration issues for the next figures. We have cooled down the concentration from room temperature to -84 degrees on the Figure 2 curve and look how the cell is able to perform on the load. Applying a load at that temperature here was not much of a success. You can see the voltage curve collapsed right away, down to 0.5 volts. But it seems that the cell became very sensitive in form of rate capacity when the cell was warmed up to -75 degrees. The voltage also recovers very fast to a healthy level of about 3.5 volts under a load of 1 MA/CM².

We have performed similar tests on larger cells but before I get there, let me show you what a double A cell again is able to do at -84. [See Figure 3] This seems to be a very critical temperature where the electrochemical behavior of the cell is almost zero.

Similar tests have been performed on larger cells like D size cells [Figure 4]. The cells in this test were precooled at 52° for 33 hours and then a load was applied of about 7/million pair per square centimeter and initially a voltage could be measured larger than 3.42 volts. This did not last too long and the voltage dropped below or close to 3 volts. The current dropped about 1.2-1.3 milliamperes total.

[Figure 5] A polarization curve of a group of D cells was obtained at different temperatures from -30° to -70°. The curve shows that at current densities of approximately half a milliampere, there is not much polarization. However, if an increase may occur in density from 0.5 to 2 million amperes

LOW TEMPERATURE PERFORMANCE TESTS

per square centimeter at -70° , a cell starts polarization and finally loses its electrochemical performance totally.

The critical temperatures, as mentioned already, seem to be in the range from -70° to 80° degrees Centigrade. At 0.5, 1, and 2 milliamperes and at 80° all the cells at these different current rates are not able to perform anymore. At 80° there is definitely a clear performance and it increases with an increase in temperature.

As Dr. Levy mentioned before, the attraction comes when you go to the larger cells that we presently build for the power systems (10,000 ampere-hour cell). We have tested this cell with cryogenic materials, under cooling and warm-up conditions and we have checked the rate capability of the cell at a constant load of 40 amperes. [Figure 7] This was not done on a single cell, it was done on a submodule, where three 10,000 ampere-hour cells are in series. That is why we have an initial voltage of close to 10 volts or 11 volts. [Figure 8] But when cooling it down you see we lose rate capability and the coolant we use was CO_2 on this large cell which weighs about 500 pounds, but it took much less time to warm it up and regain rate capability again.

We have two submodules here. [Figure 9] One is discharged to cut off at 9 volts. When the 9 volt volume has been exceeded it will disconnect from its load and the second submodule is 50% discharged--that means for roughly 5,000 ampere-hours. During cooling in CO_2 again both cells behave the same way voltage wise until it comes maybe to the last five hours in the cooling process. The 50% discharge submodule is somehow more sensitive to cooling than the 3 volt cutoff cell. This may be due to its thermoelectricity because most of the electrolyte in the "e" volt cutoff cell has been consumed. Therefore, cooling capability of that cell might not be as good as if you had waited a little longer. But at least it shows you that the discharge capability drops in form of losing voltage and it recovers quickly on the warm-up trend.

Now let's look at [Figure 10]. We have here again a full charge, that means a fresh cell, and a 50% discharge cell which are both cooled with liquid nitrogen. Furthermore, looking at the time scale it takes not quite as long as it does with solid CO_2 . We need about eight hours to free a submodule of that size so that we have almost no voltage left whatsoever. That means we spent eight hours exposing a submodule of that size to liquid nitrogen--it loses completely its electrochemical capabilities. Regardless, if fresh or charged or semidischarged, it does not make any difference. All the voltage disappears when the

LOW TEMPERATURE PERFORMANCE TESTS

temperature reaches a different level. We were not able to measure temperatures within the cell. We just were able to measure the time which is necessary to cool the submodule down.

Figure 5 is here because voltage alone might not tell us too much in form of rate capability, but this cell was pre-cooled down to Time Zero. $T=0$ is a time where the submodule was transferred from the nitrogen cooling to the CO_2 cold pack. As long as it was cooled with liquid nitrogen there was no voltage there whatsoever. When warming it up to CO_2 temperatures, we see a recovery in voltage and after we reached the plateau we tried to apply some loads (4 milliohm) to the cell. Under healthy conditions, 4 milliohm on this cell would deliver 2,500 to 3,000 amperes, but pre-cooling it down to -80° does not allow the cells to perform at room temperature conditions. That means it could not use two cells in ampere currents. We see currents here in the range of 100 million amperes or slightly larger than that. The test which we have performed should just demonstrate that if one has a faulty cell, and if you would have the capability of dumping or dropping this cell into liquid nitrogen, you would be safe from any hazardous conditions. To give you just one example of a double A cell which is dropped in liquid nitrogen, it takes eight hours before the double A cell loses its activation. People skilled in the area of manufacturing batteries, and who have realized during the activation process that they have a bad cell, suggest you drop it in liquid nitrogen to deactivate.

Thank you very much.

CONTROLLING HAZARDOUS REACTIONS DURING VOLTAGE
REVERSAL OF HIGH ENERGY LITHIUM CELLS

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We have heard several speakers discuss the problems associated with forced overdischarge of high energy lithium cells, and I would like to present, in some detail, the approach we at Altus Corporation have followed to address those problems, especially in the Li/SOCl_2 system.

Conceptually, one can consider that the active life of these cells may be limited by the anode, the cathode current collector, or the liquid oxidant, depending on the design selected by the battery engineer. As a practical matter, however, only the first two choices provide a reliable product. As we shall see, the characteristics of cells and cell components will vary significantly depending upon which design is selected.

Figure 1 shows the voltage behavior of the individual electrodes (vs. a Li/Li^+ reference electrode) and of the complete cell in the case of an anode limited design. By an anode limited design, I mean one in which the active life of cell is limited by the electrochemically available lithium. For this case, the anode polarizes towards more positive voltages causing the decline in cell voltage. A cell voltage of zero is observed when the anode potential is equal to the cathode potential. Upon continuing forced discharge, the anode is forced to voltages more positive than the cathode, and negative cell voltages are observed. The voltage fluctuations are typical of this design, and are probably caused by intermittent contact between the anode substrate and residual lithium. It is important to recognize that lithium may remain (electrochemically isolated) in such "anode limited cells".

becomes negative with respect to the Li/Li^+ reference electrode. The anode remains stable at a slightly positive potential. The principal electrochemical reactions which occur during this time are (1) the usual oxidation of Li and reduction of SOCl_2 and perhaps sulfur until the cell reaches zero volts; (2) following this, after the cathode has assumed a negative voltage, electrodeposition of lithium is permitted, whereas oxidation of SOCl_2 , AlCl_3 , and LiCl is thermodynamically prohibited.

At this point, I think we may say that there are indications that a cathode-limited design is less hazardous than an anode-limited design. But we can go much further in using the previous information to exploit some geometric and electrochemical effects to great advantage.

One additional degree of freedom which a battery engineer has is whether to design the package as a case positive or case negative cell. In the approach I will now describe, a case positive configuration is preferred.

Figure 5A is an exploded view of a case-positive cell containing a single anode and cathode. During normal discharge, the case is the positive terminal and the pin is the negative terminal. A ceramic-to-metal seal insulates the terminals from each other and forms the necessary hermetic seal. The internal resistance of the cell may be represented as $R_{S1} + R_C$. Upon forced overdischarge, the sign of each electrode will reverse and, after the cathode assumes a negative potential with respect to Li/Li^+ , metallic lithium may be plated into the cathode. This electrodeposition will occur at a certain negative cell potential, the magnitude of which depends principally on interelectrode spacing, imposed current, electrode surface area, electrolyte conductivity, and the overvoltage associated with the cathode current collector material and substrate material. Eventually, with appropriate design, Li can reportedly be made to deposit in a continuous metallic bridge spanning the anode-cathode spacing, thus forming an internal electronically conducting path. However,

Figure 2 shows the voltage behavior for the case of a cathode limited design: one in which the active life of the cell is limited by the available surface sites of the cathode current collector. In this case, the anode remains at a fairly constant voltage, while the cathode polarizes towards less positive potentials, causing the decline in cell voltage. As in the previous case, a cell voltage of zero is observed when the anode potential is equal to the cathode potential. Upon continuing discharge, the cathode is forced to voltages more negative than the anode, and negative cell voltages are observed.

It is valuable to take a closer look at the processes which occur at each electrode during forced overdischarge, and one way this can be done is by simulating each design in a three-electrode laboratory cell. An anode-limited design may be simulated by using a nickel anode and carbon cathode current collector. A 3-electrode arrangement of this type is shown in the inset of Figure 3. Initially, both the carbon electrode and the nickel anode are equally positive with respect to a Li/Li^+ reference electrode. Upon passage of current in a direction to simulate forced overdischarge, the nickel anode polarizes to a more positive potential, while the cathode polarizes to a slightly less positive potential. Both electrodes, however, remain highly positive with respect to a Li/Li^+ reference electrode. Under these conditions, the electrodeposition of metallic lithium is thermodynamically prohibited. What can and does occur at the anode is the oxidation of SOCl_2 , AlCl_3 , and LiCl to produce principally chlorine. There is some evidence reported in the literature which suggests the existence of regenerative processes.

Figure 4 represents the case of a simulated cathode limited design. The inset again shows each electrode of a 3-electrode cell. Initially, the lithium anode is at zero potential with respect to the Li/Li^+ reference electrode and the cathode current collector is at a high positive potential. Upon passage of current, the cathode - usually a glassy carbon electrode - rapidly polarizes, and eventually

there are potential hazards associated with plating lithium into a cathode current collector, particularly one filled with discharge products.

An attractive alternative, one with some distinct advantages, has been the approach we have followed for several years. Referring again to Figure 5A, it can be seen that an alternate path for the deposition of lithium and formation of a metallic bridge exists between the inner surface of the top section of the case and the top surface of the anode; this path has a resistance R_{S2} associated with it. A major advantage of this alternative path is that it is geometrically stable and can be optimized for forming an electronic shunt without affecting the design of the active cell. In other words, the parameters of importance for creation of a shunt are controlled to minimize R_{S2} with respect to the sum of R_{S1} and R_C .

One element we have successfully exploited is the particular design of the ceramic-to-metal seal. We have found that there is a substantial variation in the overvoltage associated with the electrodeposition of lithium on different substrates in SOCl_2 electrolyte. For example, deposition between electrodes separated by about 0.5 mm occurs at 0.8v on stainless steel; 0.2v on nickel; and 0.1v on copper. (These differences are probably due to different types of passivating films on each metal.) We have found it advantageous to therefore use a copper braze in the sealing of these cells. This also has the effect of promoting the deposition in a small ring, as opposed to a large plating area, a condition which favors dendritic growth. Another feature of the design is to employ a small metal piece as an anode contact member. It is of about the same diameter as the ceramic-to-metal seal, and assures that metallic lithium will be optimally available as a counter electrode during forced overdischarge.

Figure 5B shows the appearance of a cell of this design as it enters reverse voltage. The lithium is nearly consumed, exposing one side of the metal substrate. Voltage reversal has occurred, so that the case is now the negative terminal, while the anode pin is now the

positive terminal. Residual lithium remains in contact with the substrate, and it faces the area of the ceramic-to-metal seal. Under these conditions, lithium deposition originates in the outer section of the ceramic seal, and continues growing in the direction of the remaining lithium anode, eventually bridging the gap. The operation of this feature might be regarded as an "electrochemical switch" which is closed upon voltage reversal. In this fashion, the current being applied to the cell is now harmlessly passed through a solid conductive pathway, and hazardous reactions are avoided.

While this ability to control hazardous reactions is important in active battery configurations, it is particularly critical in high power reserve-activated batteries of the bipolar design. A battery of this configuration is a series arrangement of cells - one where cells are intrinsically subject to reverse voltage - but one where it is impractical to consider any external means of protection. We have therefore focused considerable attention on incorporating this feature into such batteries. Figure 6 presents the results of a demonstration of the successful operation of this electrochemical switch in a ten-cell bipolar module operating at 60 mA/cm². In this module, four of the cells were designed to be substantially more cathode limited than the remaining six cells. In this fashion, the battery could be discharged normally, and the low-capacity cells would be forced into voltage reversal by the operating cells. For this demonstration, the voltage of each cell was continuously monitored by a data-logger. In the figure, you can see that Cells #8 and 9 entered reverse voltage at about 19 minutes after the load was applied, followed by Cells #4 and 5 at about 20 minutes. All four cells stabilized at about -0.2v, while the remaining cells functioned normally at about 3 volts/cell.

The feature I have just described is incorporated in all of our LTCTM cells and battery systems. It has been extensively tested in a variety of configurations, and has proven to be a reliable method of controlling hazardous reactions associated with voltage reversal of high energy density lithium batteries. Further information can be found in U.S. Patents 4,264,688 and 4,331,745.

BEST DOCUMENT AVAILABLE

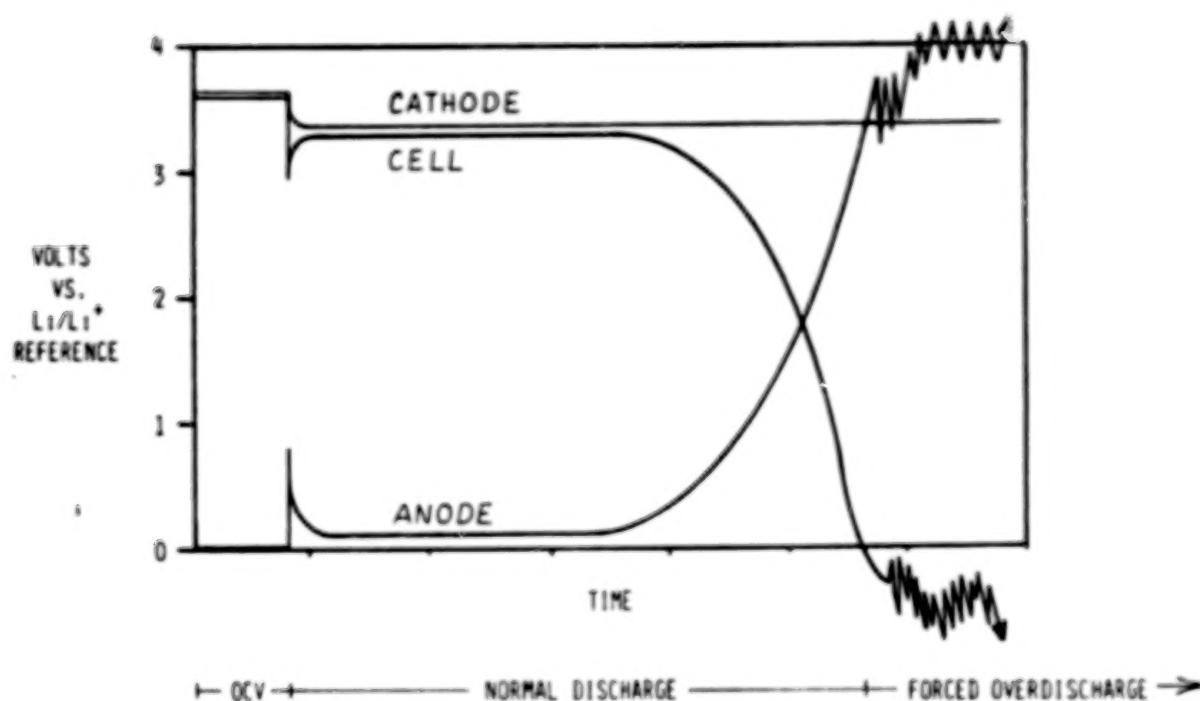


Figure 1

Li/SOCl_2 CELL: CATHODE LIMITED DESIGN

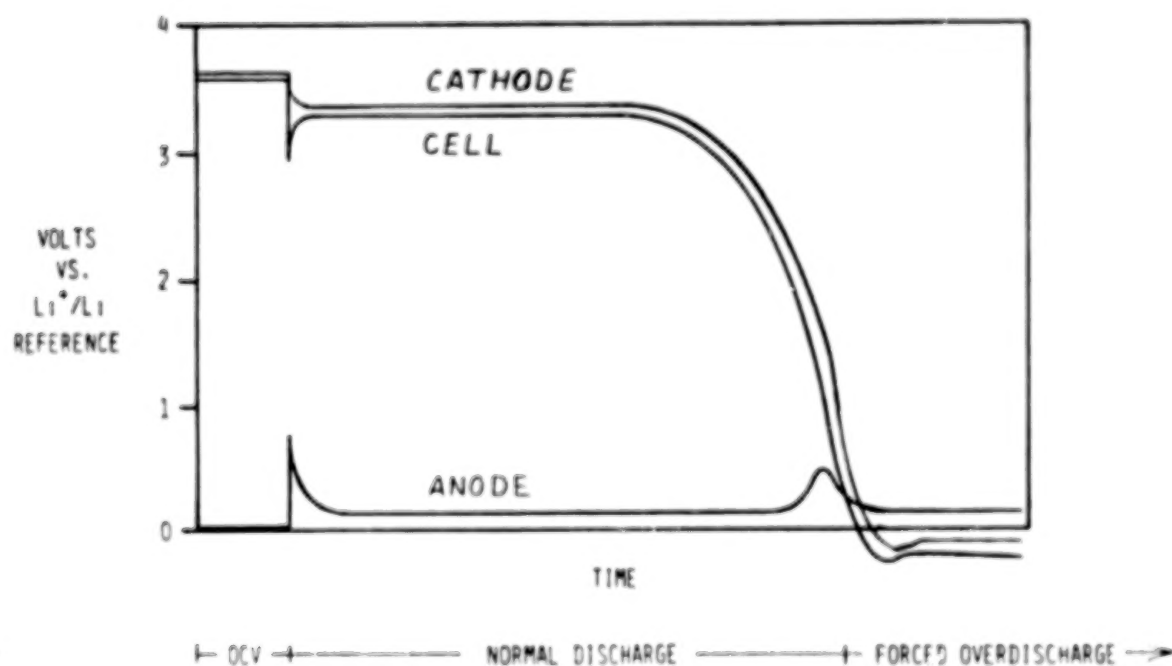


Figure 2

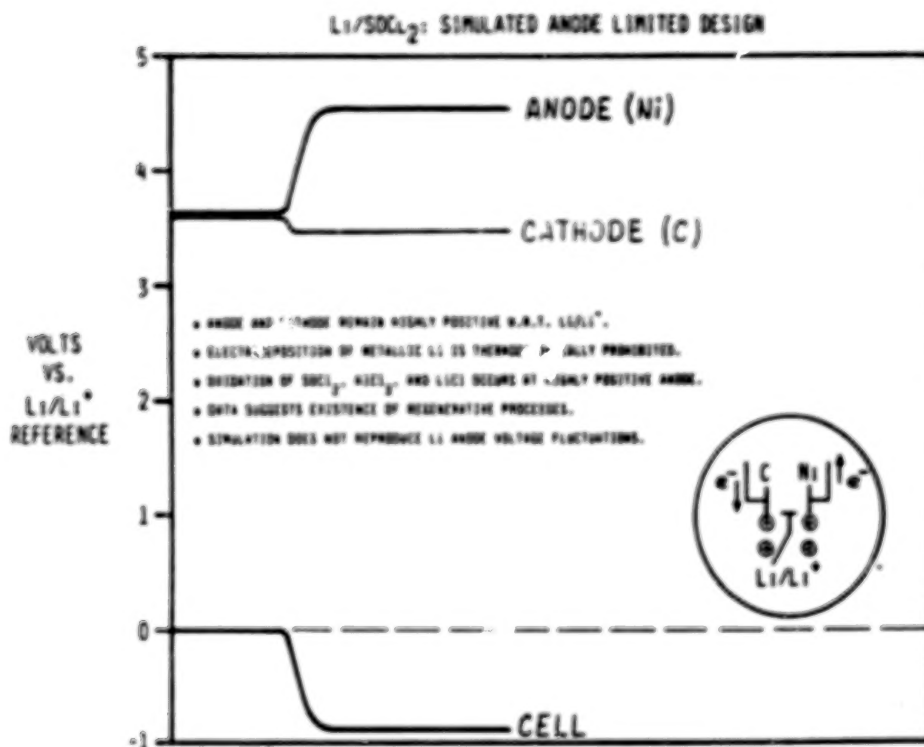


Figure 3

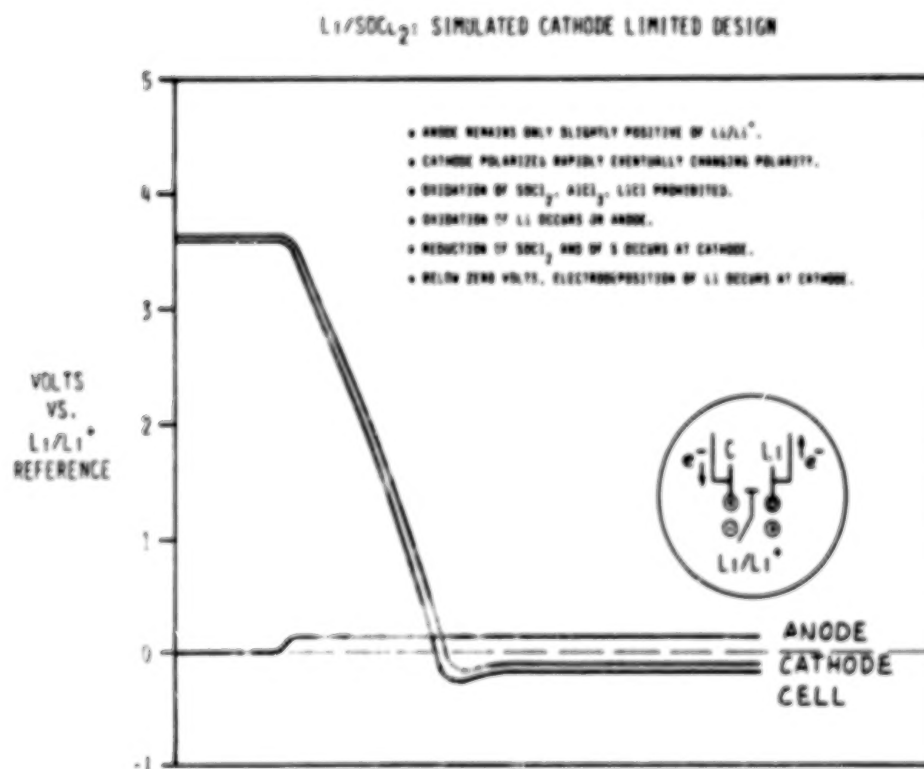


Figure 4

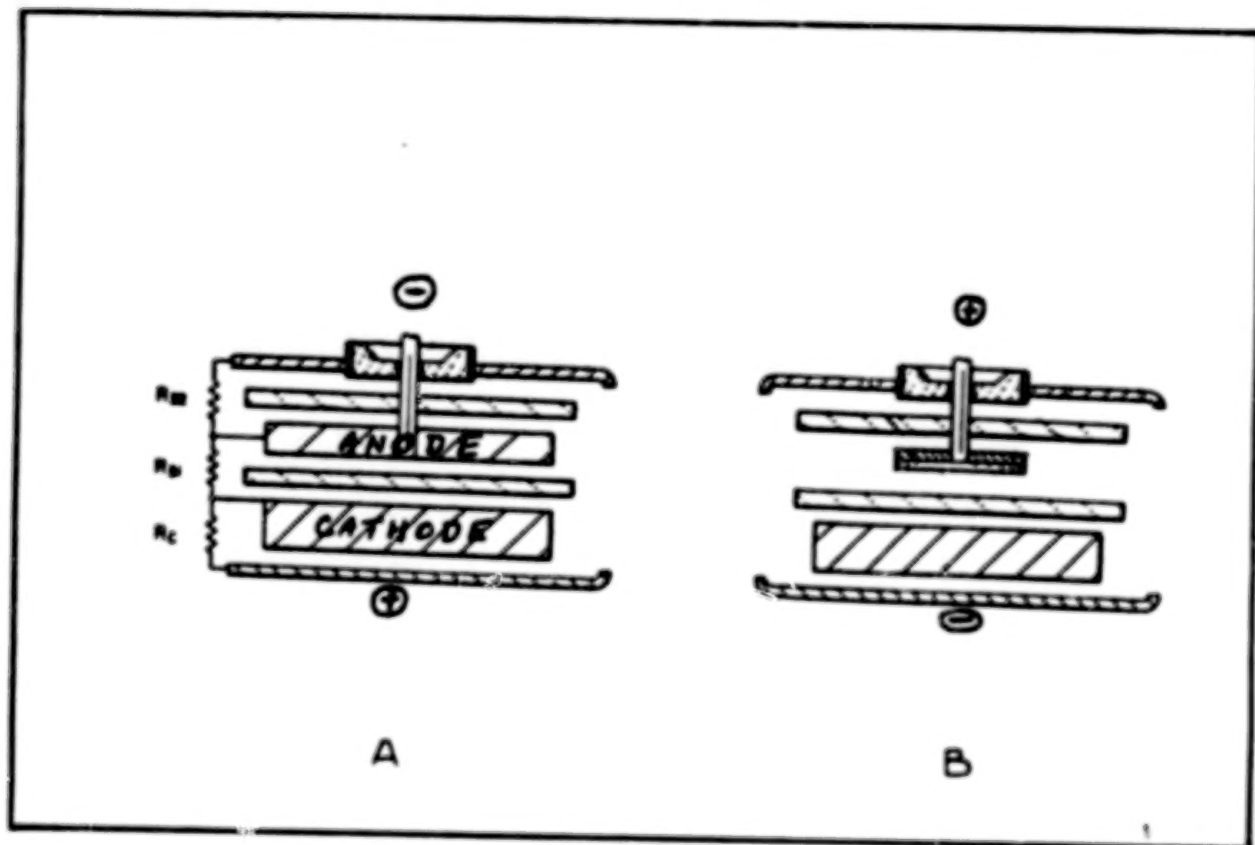
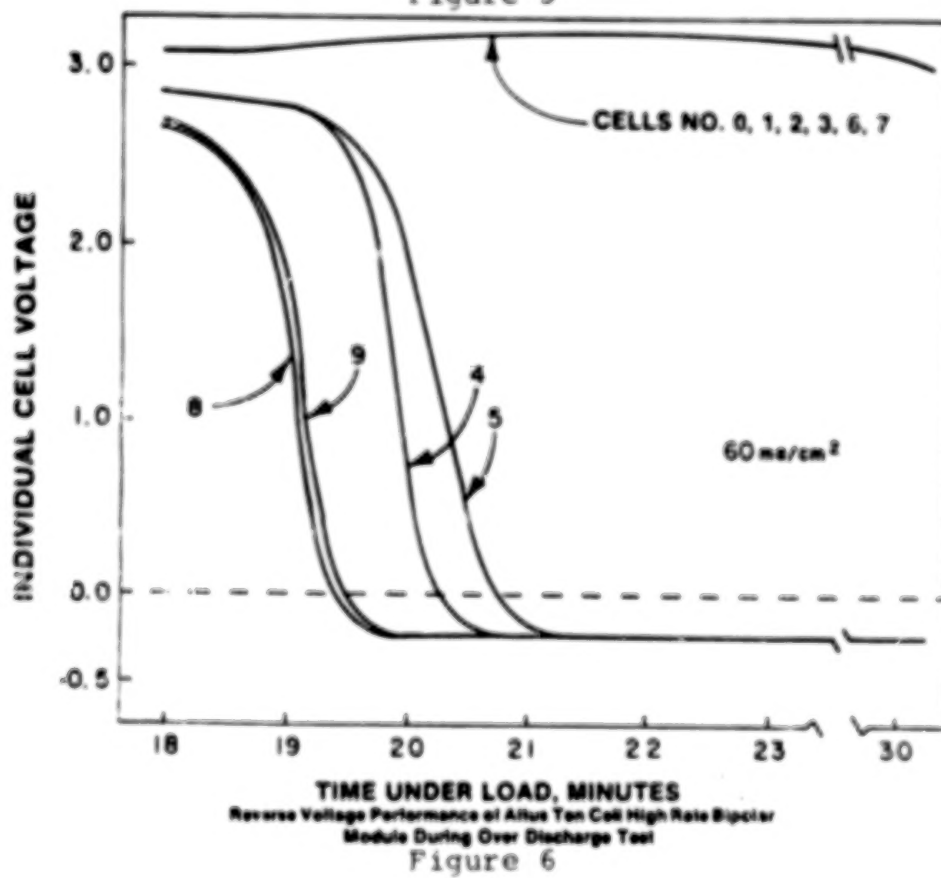
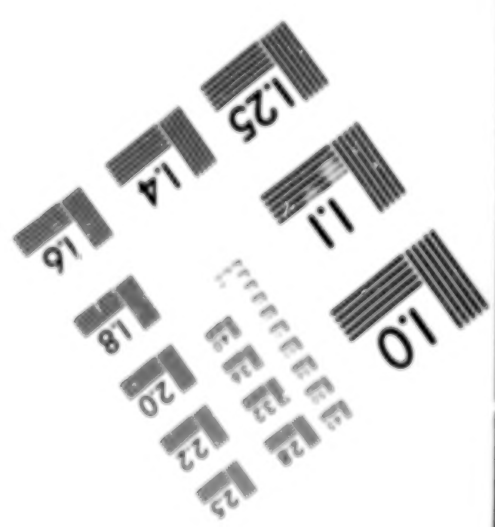
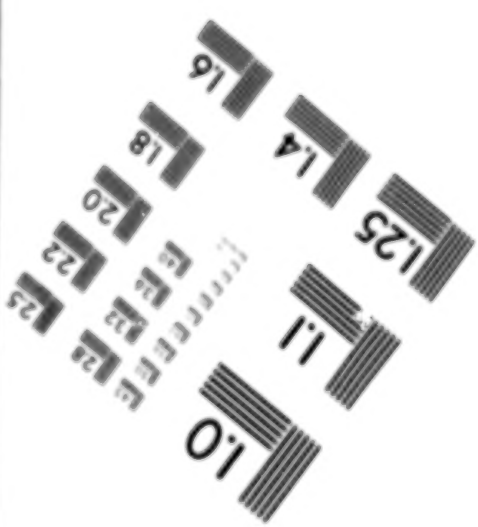
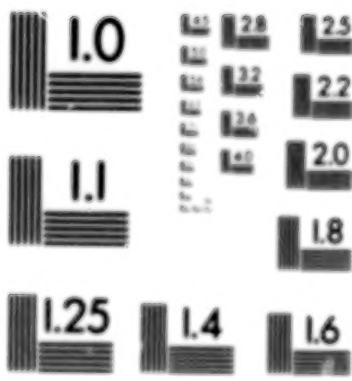
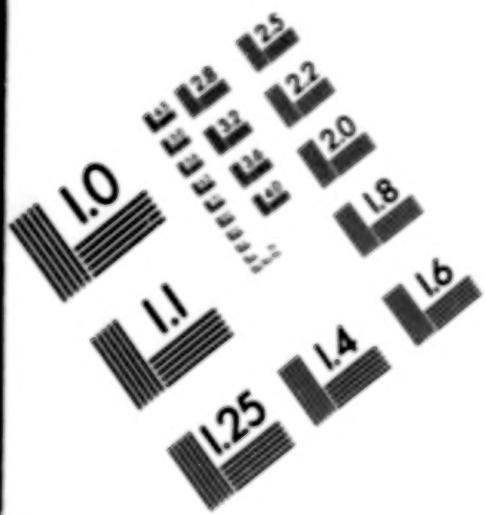


Figure 5





DESIGN OF A SAFE CYLINDRICAL LITHIUM/THIONYL CHLORIDE CELL

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D.H. JOHNSON

ABSTRACT

Cell design criteria have been established which can result in a safe lithium/thionyl chloride cell. A cell vent, a low area internal anode cell, cell balance and composition of the cathode-electrolyte solution have been found to be important factors in the design of a safe cell. In addition to routine testing, both undischarged and discharged cells have been subjected to electrical abuse, environmental abuse and mechanical abuse without disassembly.

Introduction

Batteries are electrochemical energy systems which contain reactive chemicals. The design of a safe battery must take into account the chemistry of system being used and must deal with the peculiarity of the individual system. During the evolution of both the alkaline manganese dioxide and nickel cadmium battery systems, special design and safety features were developed to render them safe for consumer use. To achieve substantially higher energy density from batteries, more aggressive chemicals have been employed and greater care in the battery design is required. Extensive testing must be conducted during the design of these batteries to insure their safety.

The lithium/thionyl chloride cell system is one of the highest energy density systems available today. The anode, lithium is a low melting metal which is oxidized during discharge. The cathode, thionyl chloride (SOCl_2), is a liquid which is reduced on a conductive carbon current collector during cell discharge. The thionyl chloride also serves as a solvent for the electrolyte salt and is in "direct" contact with the anode. The high energy density and the "direct" contact of the anode and cathode provide a potentially unstable condition which must be taken into account when designing lithium/thionyl chloride cells. A protective LiCl film forms on the anode and prevents the direct reaction of the anode and cathode. The lithium/thionyl chloride cell must be designed so that the passivating anode film is preserved whenever the cathode or other reactive material is in contact with the anode. The film may be disrupted and the cell rendered unstable if the anode is melted especially if conditions for spontaneous repair of the film are not present.

DESIGN OF A SAFE CYLINDRICAL LITHIUM/THIONYL CHLORIDE CELL (Continued)

Based on the safety and performance testing of many thousands of cells, the following factors are important in the design of small cylindrical cells that will be safe both in normal use and when abused:

- * A cell vent to prevent an energy releasing reaction between lithium and thionyl chloride.
- * A low area electrode construction which has the cathode collector in contact with the wall of the cell container (internal anode).
- * An anode limited cell balance together with design features which lead to complete anode utilization and uniform reaction product distribution.
- * Control of the composition and purity of the cathode-electrolyte solution.

Vent Release Pressure:

The vent must be designed so that it will not open during normal operating conditions which the cell may encounter but opens upon increasing internal pressure. This pressure can be from external sources such as fire or internal sources such as heat generated during charging. The vent must release before the lithium anode melts and reacts directly with the liquid cathode. Upon venting, most of the liquid cathode material is removed and is thus unavailable for reaction with the anode.

The major sources of internal cell pressure as a result of increasing temperature are the vapor pressures of the liquid cathode, the sulfur dioxide produced as a discharge product and the air or other gas trapped in the cell during construction. In addition, the liquid expansions resulting from heat increase the internal pressure.

In order to determine the normal operating pressure range for a given construction, four items need to be quantified:

- (1) Internal void volume (without electrolyte).
- (2) Electrolyte volume.
- (3) Production variations of internal void volume and electrolyte fill volume.
- (4) Changes in volume due to the discharge reaction.

DESIGN OF A SAFE CYLINDRICAL LITHIUM/THIONYL CHLORIDE CELL (Continued)

The internal cell pressure can be calculated as a function of temperature and depth of discharge for the range of anode and cathode inputs anticipated during manufacture. In these calculations, the electrolyte volume (and hence the internal void volume) and variations anticipated during construction should be quantified. Any calculation of internal pressure should take into account the changes in density and vapor pressure of the SOCl_2 and SO_2 as a function of temperature so that hydraulic pressure conditions are recognized. Although behavior of the system at the critical point of SO_2 is uncertain, the pressure derived from these calculations will give a degree of confidence that an accidental vent would not occur on standard high temperature discharge but that the cell should vent if the temperature approaches the lithium melting point.

For the cell shown in Figure I, a vent release pressure of 400-600 psig insures that the cell will safely vent for cathode and anode inputs anticipated in production. If the design features discussed below are followed, the vent will not operate during any normal use of the cell. The vent is intended only to provide protection during abuse conditions such as incineration or high rate charging. This cell, at any state of discharge, should not vent upon heating to 100°C .

Electrode Configuration:

The electrode configuration and location will have an impact upon the safety of the lithium/thionyl chloride cell. A cell which has a 1.64 cm^2 interface area per cc of internal cell volume has been found to be a cell construction which is safe and does not vent on direct shorting or over-discharge at rates up to 500 milliamperes. A high area electrode construction (spiral wound cells), unless rate limited by the separator or cathode collector, can generate a large amount of heat on electrical abuse which is not easily dissipated and may result in the localized melting of lithium on electrical abuse tests. The low area cells have a greater heat capacity and external surface area per square centimeter of electrode area and are better able to dissipate any heat generated during electrical abuse conditions.

A key factor, in the design of the cell, is the placement of the anode. If the cathode collector and liquid cathode are located next to the container wall and the lithium anode is placed at the center of the cell, then heat from an external source must be transmitted through the liquid cathode to reach the anode. This means that the internal pressure will substantially increase prior to melting the lithium. In cells where the lithium is next to the container wall, the lithium may melt and react with the liquid cathode before the internal pressure is high enough to open a vent system and evaporate the thionyl chloride. The results of open flame testing are shown in Table I for the cell construction shown in Figures I and II.

DESIGN OF A SAFE CYLINDRICAL LITHIUM/THIONYL CHLORIDE Cell (Continued)

TABLE 1

DIRECT FLAME ABUSE

Comparison of External Anode
To Internal Anode Constructions
Undischarge Cells

	<u>Internal Anode</u>	<u>External Anode</u>
Direct Flame Test (Heating Cell in) (Open 600°C Flame)	100% Normal Vent	33% Normal Vent 66% Cell Disassembly

If the external anode cell is thermally insulated, it should be able to withstand greater thermal abuse. The better the insulation the greater the abuse that the cell can withstand. Suitable insulating materials are well known to those skilled in the art.

Active Material Balance:

Active material balance of a lithium/thionyl chloride cell is the ratio of the ampere hour capacity of thionyl chloride to that of the lithium anode. Initially, it would appear that an active material balance of 1.0 would be the best for maximum cell capacity. However, the liquid cathode is continually consumed throughout the discharge of the cell via the following reaction:



Although a portion of the liquid volume is replaced with sulfur dioxide, the cell dries out on discharge. As a result, only a portion of the original area retains ionic conductivity. This problem is more severe for a deeply discharged cell such as those used at low rates of discharge. If the cell is charged or force discharged, the current density on those locally conductive areas is significantly increased to a point where local melting of the lithium could produce rapid thermal runaway. A cell vent is not effective in preventing this process. Local deficiencies in ionic conductivity may lead to hot spots under abuse. However, if the cell is balanced so that there is excess liquid cathode, and if a means is provided to maintain pressure on a uniformly absorbant separator, then these local deficiencies in ionic conductivity can be avoided. A second result of excess cathode balance and uniform electrode contact is that lithium usage is more complete and more uniform after complete discharge and reaction products are uniformly distributed. The anode grid also insures complete and uniform lithium usage.

DESIGN OF A SAFE CYLINDRICAL LITHIUM/THIONYL CHLORIDE CELL (Continued)

Composition and Purity of the Cathode-Electrolyte:

There are other factors which can affect the safety of a thionyl chloride cell. They are:

- (1) Salt concentration in the cathode-electrolyte.
- (2) Raw material purity.

An investigation was conducted to evaluate the effect of salt concentration (LiAlCl_4) between 0.75 and 2.5M on the distribution of reaction products after low rate discharge. The solid reaction product distribution was then determined as a function of distance from the anode following discharge to 0 volts on a 2000 ohm load. The data are shown in Figure 3. Low salt concentrations resulted in a build up of elemental sulfur in the separator region and in the reservoir regions of the cell. The disposition of sulfur at the separator/anode interface decreases with increasing salt concentration. It has been found that a salt concentration of 1.5 to 1.6M LiAlCl_4 in thionyl chloride is preferable based on both analytical data and safety testing of cells.

Corrosion of the lithium anode is via the following reaction:



The solid products in this case are deposited on or very near the anode. The presence of water, acids and organics in the electrolyte causes corrosion thus increasing the likelihood that the cell will be unsafe if abused electrically or by heating. Control of the purity of the cathode-electrolyte is necessary.

Extensive abuse testing of thousands of cells made with these design criteria have been completed. As discussed above, these tests include electrical abuse, environmental abuse and mechanical abuse of undischarged and discharged cells. Cells were discharged at 71°, 21° and -40°C. No cell disassemblies were observed on any of these tests. Further testing is still being conducted. However, the results of tests conducted to date indicate that a safe cylindrical lithium/thionyl chloride cell can be made if properly designed.

APPENDIX I

Small cylindrical cells constructed, as shown in Figure I, and incorporating the design features discussed in the text were subjected to a series of abuse tests. There were three types of abuse tests:

- (1) Electrical abuse - including charging, short circuit and overdischarge.
- (2) Environmental abuse - including incineration, hotplate and sand bath tests and water immersion.
- (3) Mechanical abuse - including cutting, crushing, smashing, puncturing, dropping and shock and vibration tests.

Rated capacity of the cells was 1.1 amp-hrs when discharged on a 250 ohm load. In total, more than 8,000 cells were safety tested to arrive at the current design which gives the results shown in Tables I, II, and III. Cells were subjected to these tests in the undischarged, 50% discharged and 80% discharged conditions. Test results indicated that the fresh and 80% discharged cells represented the worst test condition and testing was concentrated on these cells. Normally a five cell sample was replicated on three separate occasions. On the more severe tests such as flame tests and high rate electrical abuse, larger samples were replicated a greater number of times.

<u>Test</u>	<u>Observed Effect</u>	<u>Comments</u>
I. <u>Electrical Abuse</u>		
1) <u>Direct Short at 21°C</u>		
a) Undischarged	None	3 amperes maximum
b) Discharged (80%)	None	
2) <u>Direct Short at 71°C</u>		
a) Undischarged	None	5 amperes maximum
b) Discharged (80%)	None	
3) <u>Charge Test</u>		
a) Undischarged		If cell vents, some release of SOCl ₂ will occur.
1.5 A/24 hrs.	Cell Venting ~30 min.	
1.0 A/24 hrs.	Some Venting	
500 mA/24 hrs.	None	
250 mA/24 hrs.	None	
100 mA/24 hrs.	None	
b) Discharged (80% 250 ohms)		
1.5 A/24 hrs.	Cell Venting	Same as above
1.0 A/24 hrs.	Cell Venting	
500 mA/24 hrs.	Cell Venting	
250 mA/24 hrs.	None	
100 mA/24 hrs.	None	
	5 min.	
4) <u>Forced Discharge</u>		
Undischarged and Discharged		
100 mA/24 hrs.	None	Cell heats to ~40°C
250 mA/24 hrs.	None	Cell heats to ~40°C
500 mA/24 hrs.	None	Cell heats to ~40°C

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<u>Test</u>	<u>Observed Effect</u>	<u>Comments</u>	
II. <u>Environmental Abuse</u>			
1) <u>Water Bath</u>			
a) <u>Discharged</u>		Some evolution of gas and corrosion of cell container.	
Fresh water	None		
Salt water	None		
Direct short in salt water	None		
b) <u>Undischarged</u>		Some evolution of gas.	
Fresh water	None		
Salt water	None		
Direct short in salt water	None		
2) <u>Propane Torch* (Localized)</u>			
a) <u>Seal Area</u>		When cell vents, some release of SOCl ₂ fumes occurred along with melting of the seal.	
Undischarged	Cell Venting 20 sec.		
Discharged (50%)	Cell Venting "		
Discharged (80%)	Cell Venting "		
b) <u>Bottom of Can</u>		Same as above	
Undischarged	Cell Venting 30 sec.		
Discharged (50%)	Cell Venting "		
Discharged (80%)	Cell Venting "		
c) <u>Side of Can</u>		Same as above	
Undischarged	Cell Venting 45 sec.		
Discharged (50%)	Cell Venting "		
Discharged (80%)	Cell Venting "		
3) <u>Open Flame Test (600°C)*</u>			Same as above
Undischarged	Cell Venting		
Discharged (50%)	Cell Venting		
Discharged (80%)	Cell Venting		
4) <u>Sand Bath (Slow Heating to 250°C)*</u>			Same as above
Undischarged	Cell Venting 15 min.		1 hour heating to 250°C
Discharged (50%)	Cell Venting "		
Discharged (80%)	Cell Venting "		
5) <u>Hot Plate 210°C (Cell on Side)*</u>			
Undischarged	Cell Venting		Cell Temp. 160°C Plate Temp. 210°C
Discharged (50%)	Cell Venting		
Discharged (80%)	Cell Venting		
6) <u>Opened Cell (Dropped in Water)</u>			Some reaction and evolution of gas in water.
Undischarged	None		
Discharged (50%)	None		
Discharged (80%)	None		
7) <u>Opened Cell (Exposed to Fire)</u>			
Undischarged	None		
Discharged (50%)	None		
Discharged (80%)	None		

* On any heating test, finishing a cell into a battery construction may extend the time to venting.

<u>Test</u>	<u>Observed Effect</u>	<u>Comments</u>
III. <u>Mechanical Abuse</u>		
1) <u>Abuse and Curiosity</u>		
a) <u>Cut with Saw</u>		When the cell container is broken, some release of SOCl ₂ . Possible sparks if cut quickly.
Undischarged	None	
Discharged (50%)	None	
Discharged (80%)	None	
b) <u>Crush with Vise</u>		Same as above
Undischarged	None	
Discharged (50%)	None	
Discharged (80%)	None	
c) <u>Crush with Hammer</u>		Same as above
Undischarged	None	
Discharged (50%)	None	
Discharged (80%)	None	
d) <u>Puncture with Nail</u>		Same as above
Undischarged	None	
Discharged (50%)	None	
Discharged (80%)	None	
2) <u>Drop Test</u>		
a) <u>Undischarged</u>		Some cell denting occurred
6 feet	None	
20 feet	None	
60 feet	None	
b) <u>Discharged (50%)</u>		Some cell denting occurred
6 feet	None	
20 feet	None	
60 feet	None	
c) <u>Discharged (80%)</u>		Some cell denting occurred
6 feet	None	
20 feet	None	
60 feet	None	
3) <u>Shock and Vibration*</u>		
a) Undischarged	None	
b) Discharged (50%)	None	
c) Discharged (60%)	None	

* Military Spec. MIL-B-180
4.7.11.1
4.7.12.1

LI-SOCl₂ CELL

Internal Anode

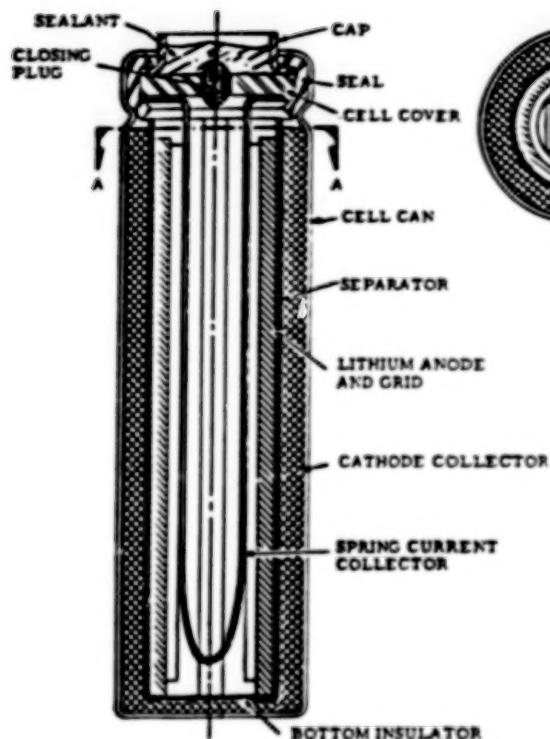


Figure 1

LI-SOCl₂ CELL

EXTERNAL ANODE

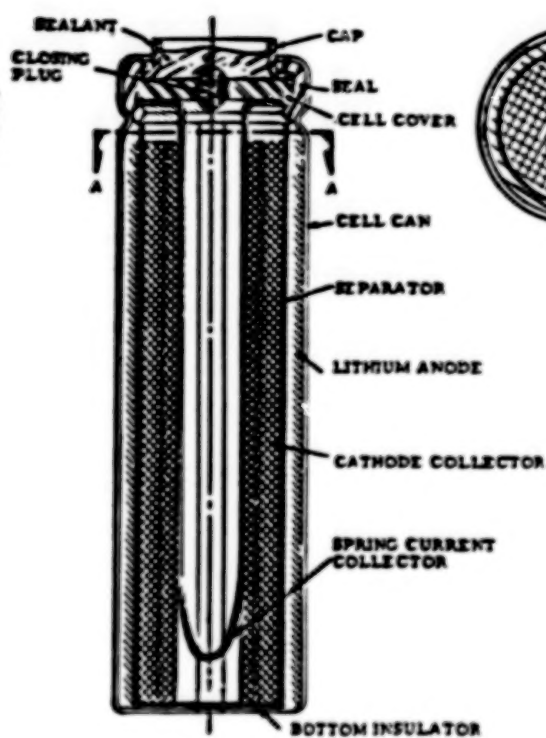


Figure 2

Deposition of Sulfur as a Function of Salt Concentration

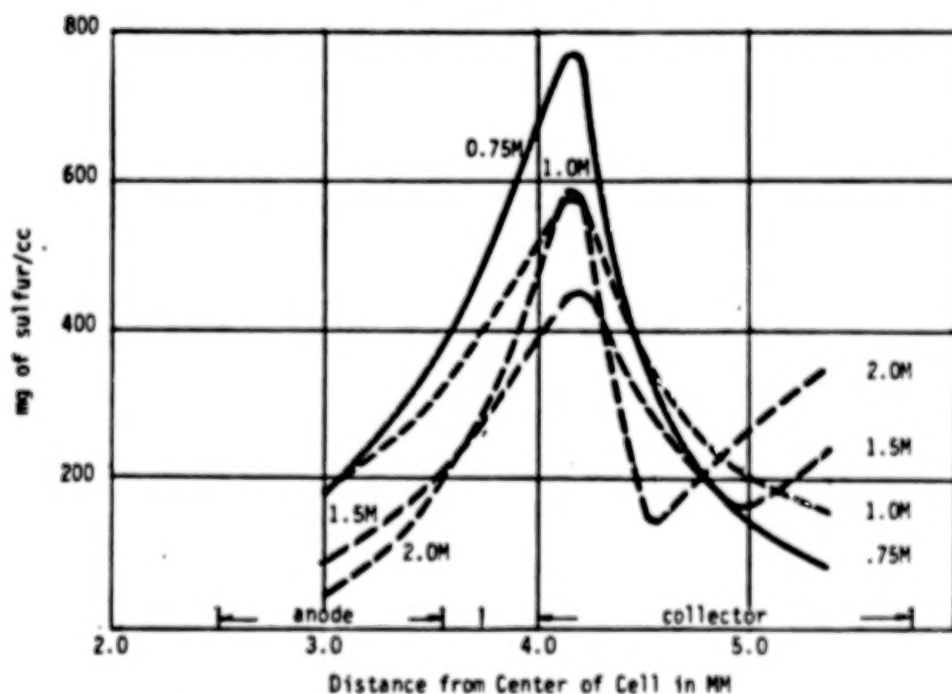


Figure 3

VALIDATING CELL/BATTERY SAFETY

NASA/GSFC BATTERY WORKSHOP

16 November 1982

BY

Dr. David Chua

Honeywell Power Sources Center

104 Rock Road

Horsham, PA 19044

PROBLEM: LACK OF STATISTICAL DATA BASE

- O NUMBER OF TESTS PER HAZARD
- O VARYING APPLICATIONS
- O FUNDING - NEVER ENOUGH
- O REAL TIME (i.e., SAFETY AFTER STORAGE)

SOLUTION: THREE STEPS

- O STEP I - COMBINE ANALYTICAL TECHNIQUES WITH CONVENTIONAL HARDWARE TESTS.
- O STEP II - USE DATA TO ESTABLISH SAFE OPERATING LIMITS.
- O STEP III - CONTROL CELL/BATTERY WITHIN SAFE OPERATION LIMITS.

STEP I: COMBINATION ANALYTICAL TECHNIQUES WITH CONVENTIONAL HARDWARE/APPLICATION TESTS

SUCH AS:

- O AC IMPEDANCE
- O MICROCALORIMETRY
- O ACCELERATING RATE CALORIMETRY (ARC)

STEP II: USE DATA TO ESTABLISH SAFE OPERATING LIMITS

- O CELL ELECTROCHEMISTRY
- O DEFINE CELL PERFORMANCE PARAMETERS
- O DEFINE BATTERY/SYSTEM PARAMETERS

STEP III: CONTROL CELL/BATTERY WITHIN SAFE OPERATING LIMITS

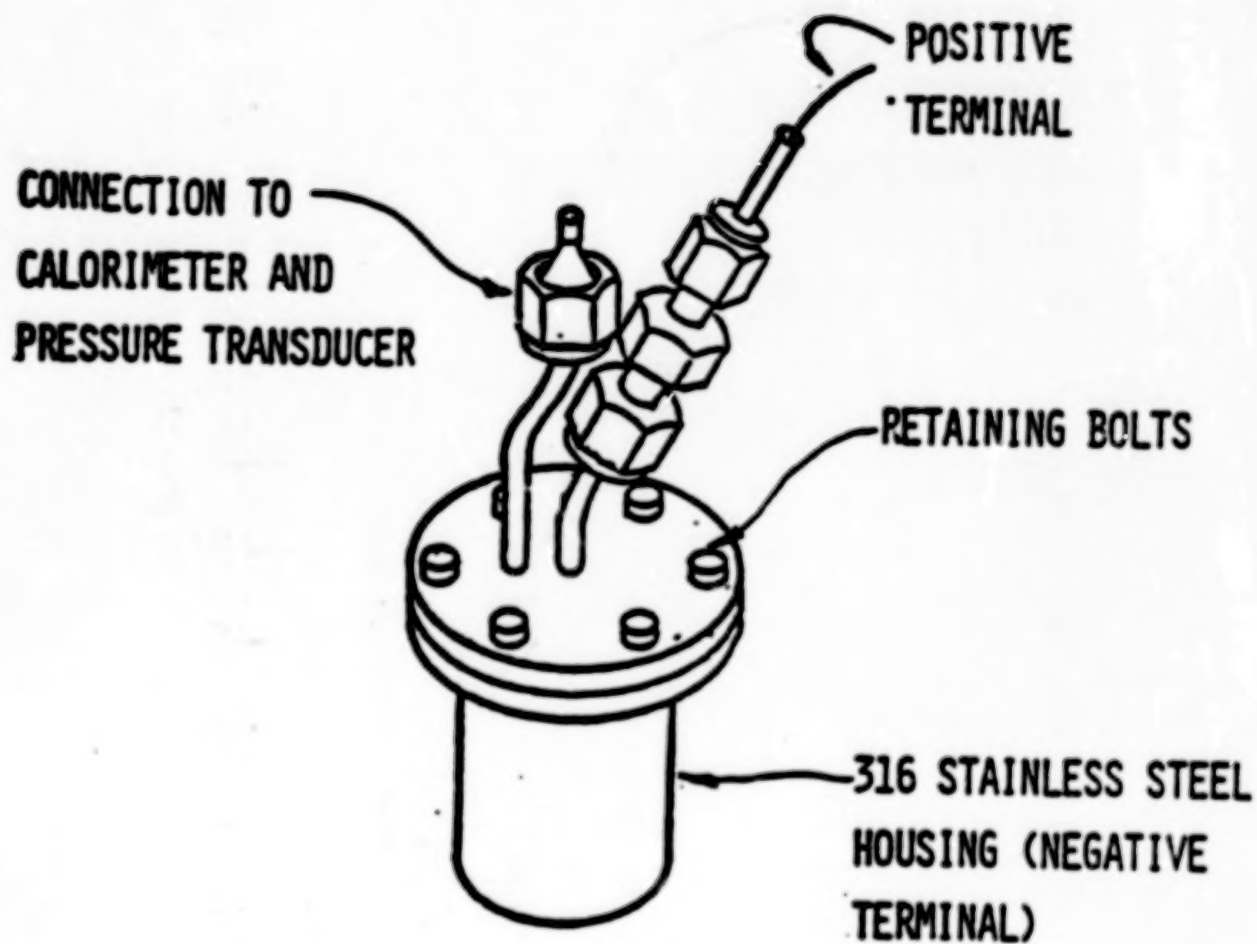
O DESIGN

- CELL
- BATTERY
- SYSTEM

O MANUFACTURING TOLERANCES

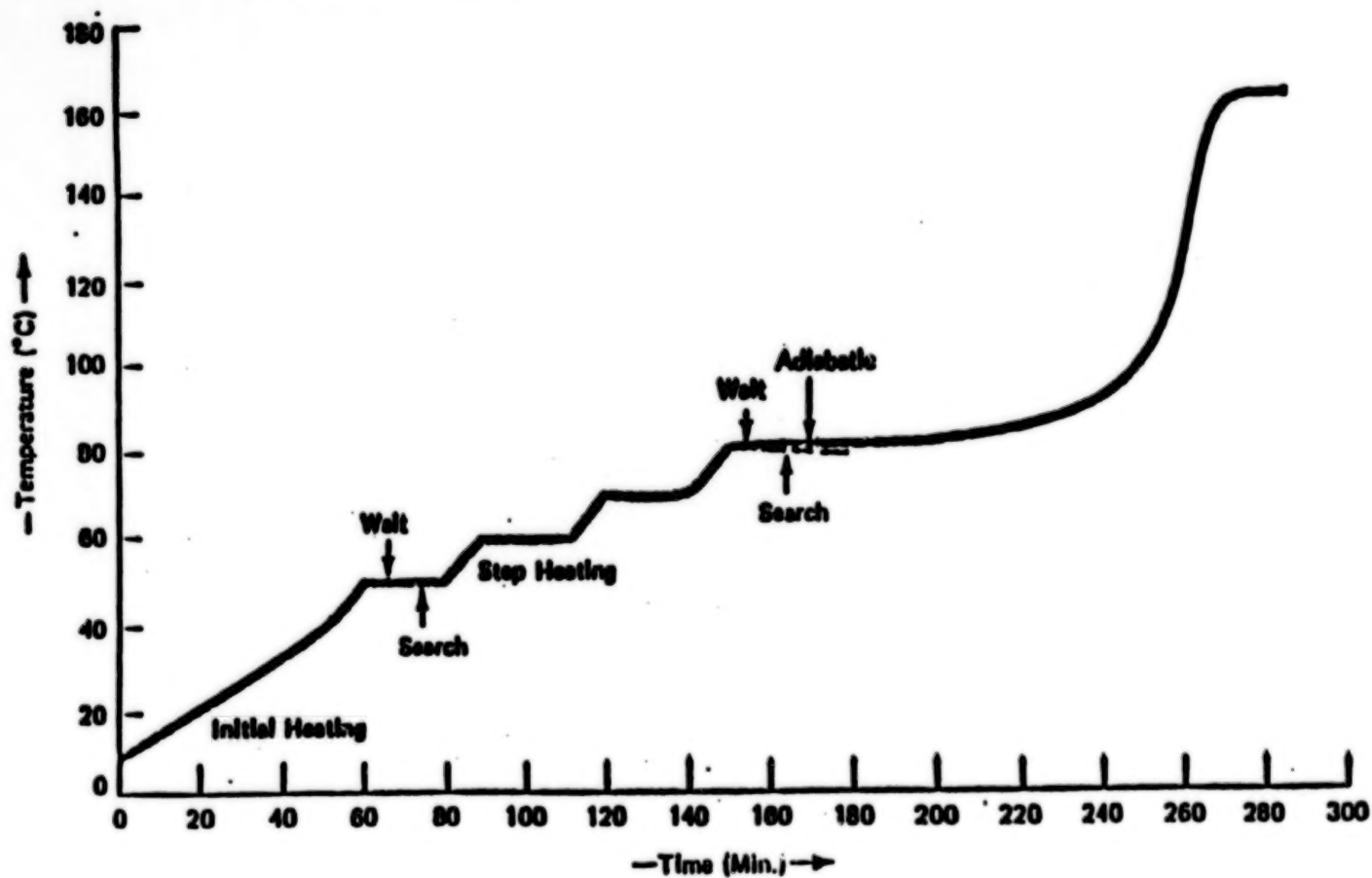
- OFF THE SHELF VS PRECISION

ARC Li/SO_2 CELL HARDWARE



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THE HEAT-WAIT-SEARCH OPERATION MODE OF AN ACCELERATING RATE CALORIMETER



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HONEYWELL IS CONTRACTED BY NSWC TO STUDY THE THERMAL AND PRESSURE BEHAVIOR OF EXOTHERMIC REACTIONS IN THE Li/SO_2 SYSTEM

- O FORCED OVERDISCHARGE AT AMBIENT TEMPERATURE.
- (RESISTIVE OVERDISCHARGE AT AMBIENT TEMPERATURE.
- O DISCHARGE AT -35°C .
- O FORCED OVERDISCHARGE AT -35°C .

CELL DESIGN DESCRIPTION

16	<u>Design No.</u>	<u>Li/SO₂ Ratio</u>	<u>SO₂/C Ratio</u>	<u>Li/C Ratio</u>	<u>Design Description</u>
	I	0.5	1.25	0.625	Lithium Limited
	II	1.0	1.25	1.25	Coulombically Balanced (Baseline)
	III	1.0	0.5	0.5	Excess Carbon
	IV	1.5	1.25	1.875	Excess Lithium

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91

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HAZARD ANALYSIS SUMMARY OF THE FOURTEEN TEST CELLS (1)

Cell Group	Cell No.	Cell Design	Test Conditions	Current Density, mA/cm ²	Test Temp., °C	Temp. Rise, °C	Max. Temp. Rate, °C/min	Pressure Rise, psia	Max. Pressure Rate, psia/min	Hazard Rating
A	I-1	Lithium Limited	Forced Overdischarge	1.0	25	-	-	-	-	-
"	II-1	Coulombically Balanced	" "	"	"	-	-	-	-	-
"	III-1	Excess Carbon	" "	"	"	-	-	-	-	-
"	IV-1	Excess Lithium	" "	"	"	202	0.34	490	1.4	Venting
B	I-2	Lithium Limited	Forced Overdischarge	3.0	25	182	0.33	(2)	(2)	(2)
"	II-2	Coulombically Balanced	" "	"	"	210	0.12	169	0.24	Venting
"	III-2	Excess Carbon	" "	"	"	273	0.56	129	0.54	Venting
"	IV-2	Excess Lithium	" "	"	"	306	4.0	171	0.17	Venting
C	I-3	Lithium Limited	Resistive Overdischarge	5 ohm load	25	212	0.63	168	7.1	Venting
"	II-3	Coulombically Balanced	" "	"	"	(2)	(2)	(2)	(2)	(2)
"	III-3	Excess Carbon	" "	"	"	287	2.1	421	5.9	Venting
"	IV-3	Excess Lithium	" "	"	"	299	0.34	220	3.7	Venting
D	II-5	Coulombically Balanced	Discharge to 2V	3.0	-35	243	17.7	1436	245	Explosion
"	II-6	" "	Forced Overdischarge	"	"	213	199.5	840	1730	Explosion

Notes: (1) The temperature and pressure increases reported in this table represent the increases observed from the start of the first exotherm detected to the end of the last exotherm observed even though these exotherms may not have occurred continuously during the experiment.

(2) Because of cell leakage problems, the data are incomplete.

CELL STATUS AT END OF DISCHARGE TO 2.0 VOLT CUTOFF VERSUS EXOTHERMIC
BEHAVIOR DURING OVERDISCHARGE FOR THE CELLS TESTED AT AMBIENT TEMPERATURE

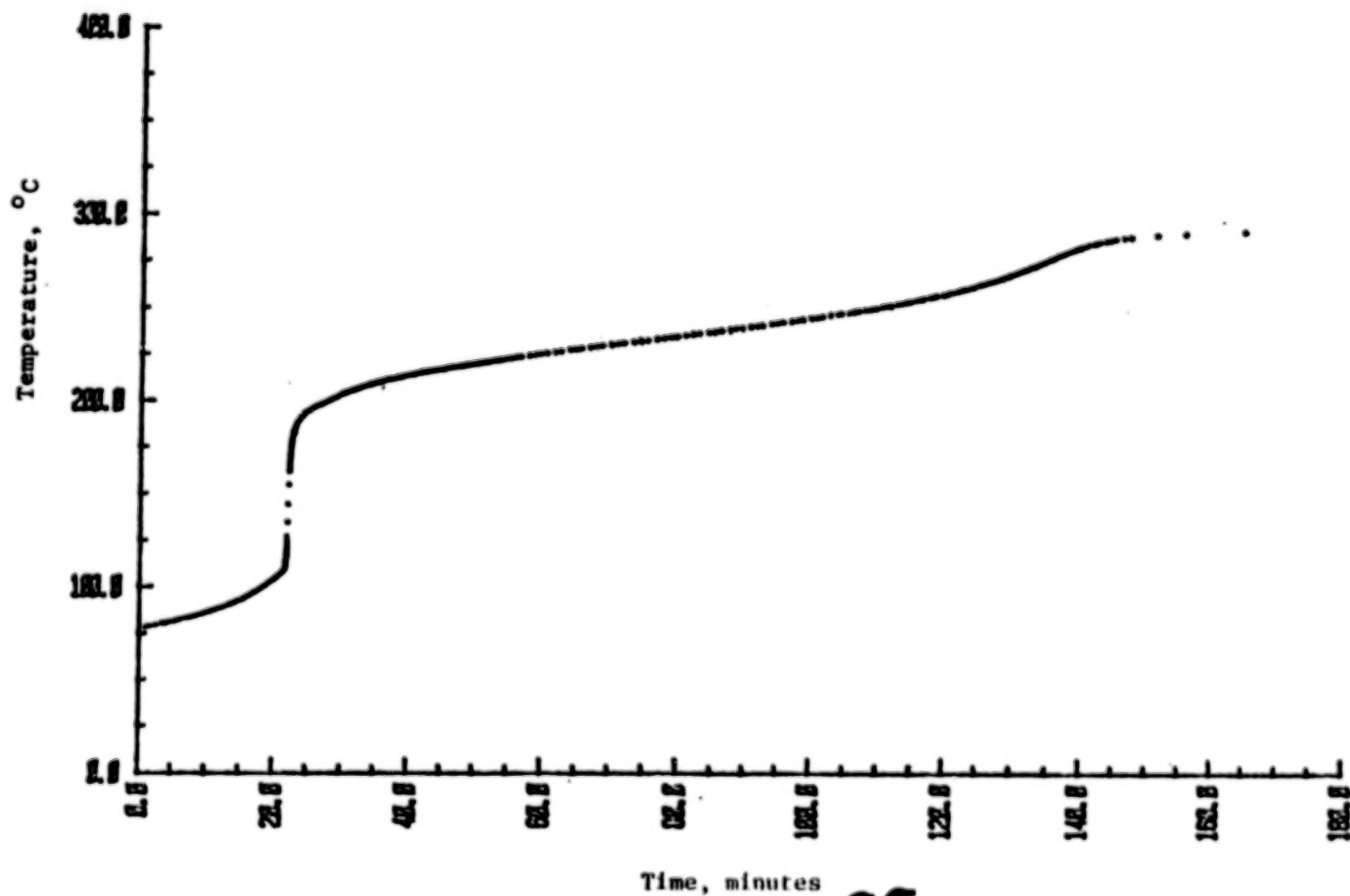
Cell No.	Discharge Current Density, mA/cm ²	SO ₂ /Li	SO ₂ /Li Area, mg/cm ²	Overdischarge Test Mode	Exotherms During Overdischarge
I-1	1.0	11.3	31.3	Constant Current	No
II-1	1.0	3.0	13.8	"	No
III-1	1.0	2.0	17.4	"	No
IV-1	1.0	0.19	6.4	"	Yes
I-2	5.0	7.0	41.5	Constant Current	No
II-2	5.0	1.1	23.0	"	Yes
III-2	5.0	1.7	25.5	"	Yes
IV-2	5.0	0.44	25.2	"	Yes
I-3	4.6	8.5	30.9	Resistive (5 ohms)	No
II-3	5.3	0.87	22.8	"	No
III-3	4.4	1.3	24.3	"	No
IV-3	5.5	0.43	22.8	"	Yes

SUMMARY OF EXOTHERM DETECTED DURING THE HEAT AND SEARCH TESTING OF CELL NO. II-6 (COULOMBICALLY BALANCED)

Initial Temperature, °C	77.48
Initial Pressure, psig	41.1
Initial Temperature Rate, °C/min	0.804
Final Temperature, °C	290.54
Final Pressure, psig	880.6
Maximum Temperature Rate, °C/min	199.5
Maximum Pressure Rate, psig/min	1730
Temperature Rise, °C	213.1
ΔH, cal	2518
Pressure Change, psig	839.5
Projected Final Temperature for Li/SO ₂ "D" Cell, °C	474.0
Projected Temperature Rise for Li/SO ₂ "D" Cell, °C	396.6

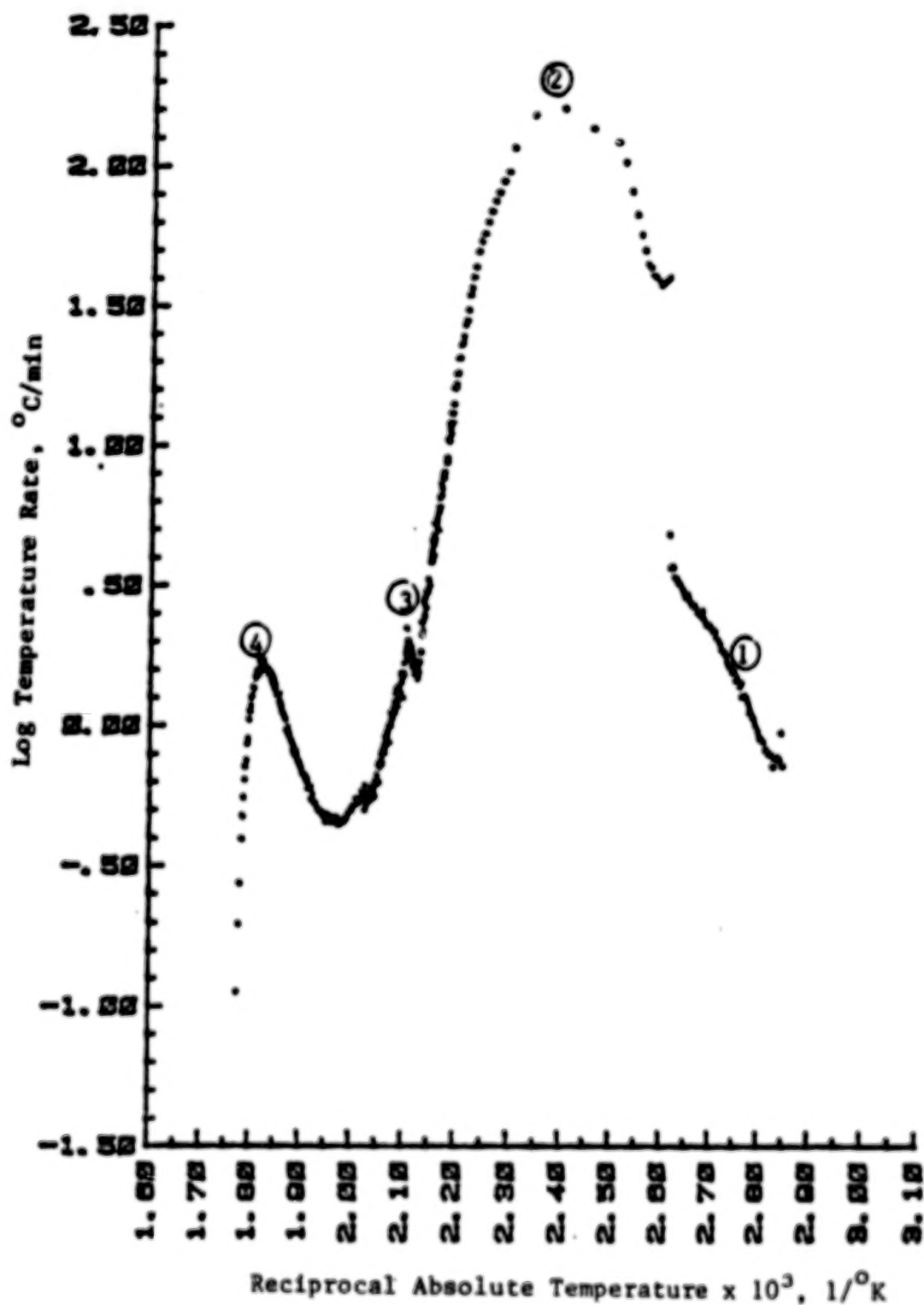
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TEMPERATURE VERSUS TIME PLOT FOR THE EXOTHERM DETECTED DURING THE
ARC ANALYSIS OF CELL NO. 11-6 (COULOMBICALLY BALANCED)



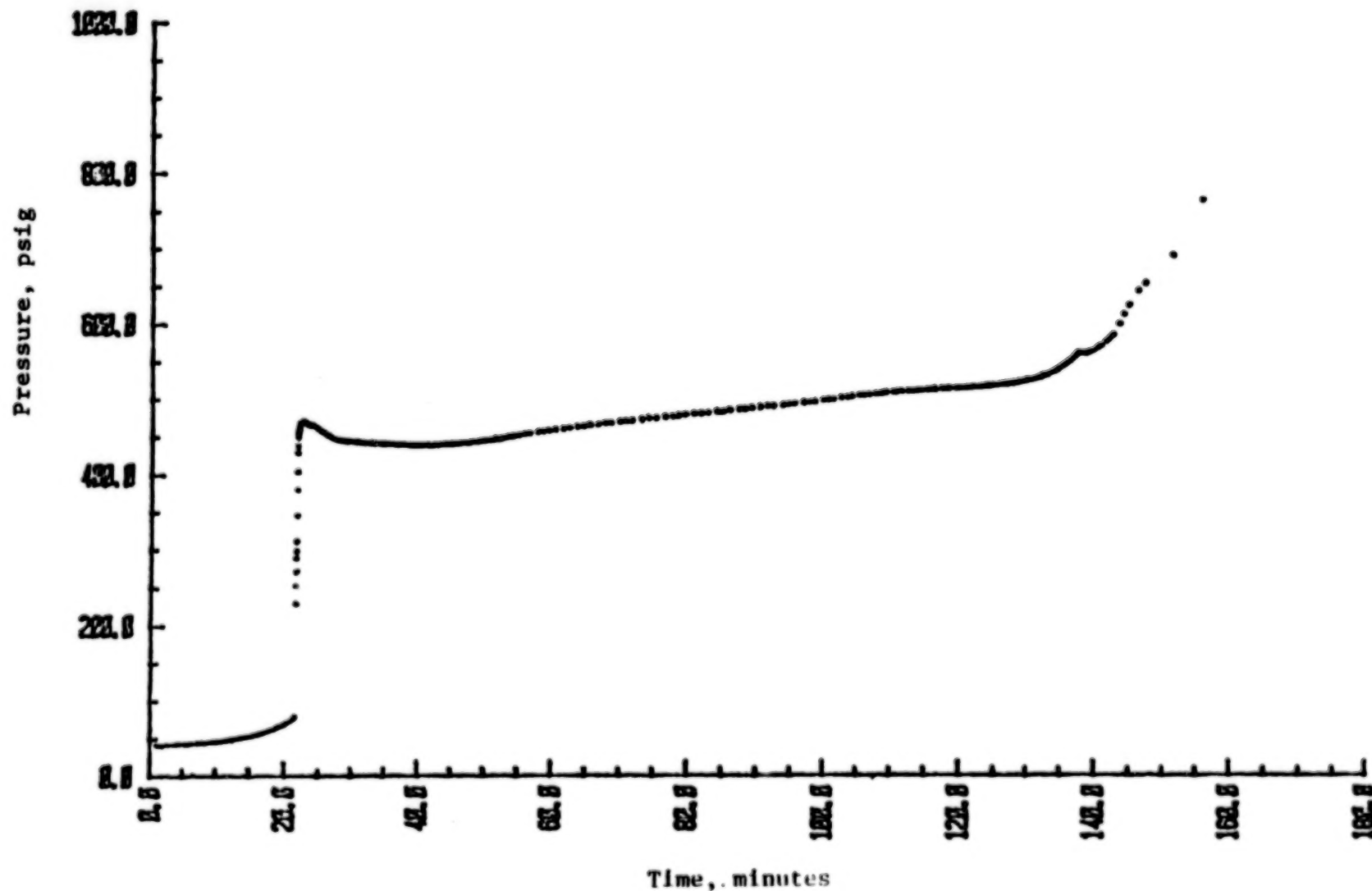
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LOG TEMPERATURE RATE VERSUS $1/T$ PLOT FOR THE EXOTHERM DETECTED DURING THE ARC ANALYSIS OF CELL NO. II-6 (COULOMBICALLY BALANCED)



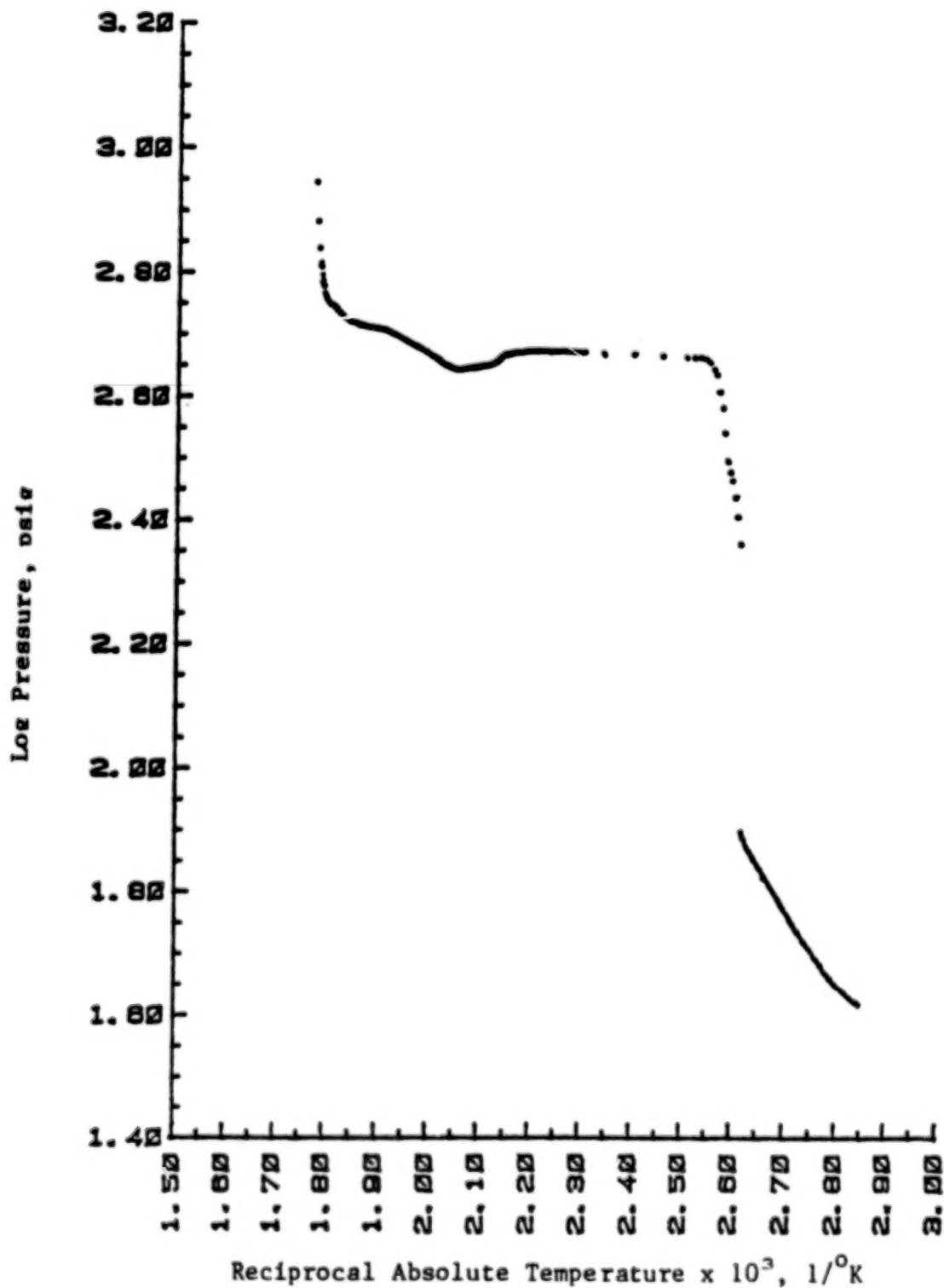
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LOG TEMPERATURE RATE VERSUS 1/T PLOT FOR THE EXOTHERM DETECTED DURING THE
ARC ANALYSIS OF CELL NO. 11-6 (COULOMBICALLY BALANCED)



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LOG PRESSURE VERSUS $1/T$ PLOT FOR THE EXOTHERM DETECTED DURING THE ARC ANALYSIS OF CELL NO. II-6 (COULOMBICALLY BALANCED)



CONCLUSIONS

USING THE ACCELERATING RATE CALORIMETER, THE HAZARDS ASSOCIATED WITH EXOTHERMIC REACTIONS OCCURRING IN Li/SO_2 CELLS UNDER THE CONDITIONS OF DISCHARGE, FORCED OVERDISCHARGE, RESISTIVE OVERDISCHARGE, AND FORCED OVERDISCHARGE AT LOW TEMPERATURES HAVE BEEN QUANTITATIVELY DEFINED IN TERMS OF:

- 1) RATE OF PRESSURE GENERATION
- 2) OVERALL PRESSURE RISE
- 3) RATE OF TEMPERATURE RISE
- 4) OVERALL HEAT GENERATION

CONSISTENT WITH THE FINDINGS OF OTHER INVESTIGATORS, WE BELIEVE THAT THE MAJOR REACTIONS CONTRIBUTING TO Li/SO_2 CELL EXOTHERMICITY ARE:

- 1) THE LITHIUM/ACETONITRILE REACTION
- 2) THE THERMAL DECOMPOSITION OF LITHIUM DITHIONITE
- 3) THE LITHIUM/SULFUR REACTION

SESSION I

DISCUSSION

Q. Halpert, GSFC: Can lithium SO₂, thionyl-chloride or sulfuryl-chloride or BCX for that matter be made safe enough for military aerospace and consumer use? I would like to address this question to the panel and ask them to give us their feelings on the issue. Secondly, if there are safety steps that the user can take to use lithium cells, what are they? And the third question is, do we have to solve problems of overdischarge safety before these cells can be used?

COMMENT

Bro, Southwest Electrochemical Company: According to what we heard today I think that alkaline batteries have a very bright future. I think the lithium batteries we have seen have been small cells. I think there the Japanese will show us the way. If you look at a publications journal called the "Echo" I think it shows that the Japanese are leading in many of the areas of consumer electronics. I think you are going to see small lithium batteries growing into the consumer electronic area primarily as an EOM product. When it comes to larger sizes I think safety is a problem which has been inadequately studied from the point of the consumer. I think that profit margins are going to be very small and not negative for manufacturers. So I wouldn't hold my breath.

COMMENT

Bis, NSWC: Well my approach is this. Again, I'll make no comments on consumer markets. All I'll do is get into trouble on that one. First of all in the Navy, yes, I think they can be made safe enough at the systems level. We do not have an approach at the cell level or battery level. We look at them to see which one would be the best choice for a particular applications. The Navy applications are so wide and so diverse and as I mentioned this morning, slight modifications of the chamber can cause violent ventings, ruptures, etc. I would like to make one other comment that Harry Taylor made that he feels we overtest these things. I don't believe we are overtesting.

8

The philosophy is that we have gotten into trouble and we cannot prevent, for example, internal cells shorts. We have had systems with internal cell shorts with SO₂ and it was only through system interaction with batteries that we were able to prevent a catastrophic runaway. So I stand very firm; I don't believe we are overtesting. As far as pegging the voltage at the voltage of the battery I agree with that technique. However, let's look at the low temperatures. We've had paper after paper in here where if these cells, balanced or unbalanced, particularly SO₂, are discharged at low temperatures to two volts as in the case that Dave Chua presented or in voltage reversal and subsequently warmed up the point where we could get into catastrophic situations. Hell, that's the real world. The Marines go out and it's cold outside and they come into a hot tent and they have battery packs on their back. These batteries get used, abused they sit around, they are turned back on and everything else. If you think consumers can abuse it, you haven't seen anything until you give it to the Marines or the Navy. I mean it's a pussycat problem with the consumer. My feeling is that if you take, and I think that that has been addressed both by GSFC, (NASA) and by Dave, the systems approach, proper integration of the battery with the system, but it has to be all the way through. I think we can use them in a safe and reliable manner with the military

- Q. Taylor, Duracell: If you were asked the same question about an alkaline battery would you give the same answer? If I were to run an alkaline battery and run an incineration test I would get into an explosion.
- A. Bis, NSWC: Yes, they all have their problems but with an alkaline if I do get into a serious runaway situation I don't have the amount of toxic gases coming off that I have with the lithium liquid cathode cells. I don't have the rate capability that I have with the alkaline. I don't have the problem, for example, of driving into the voltage reversal and subsequently warming it up and possibly, and I use the word possibly, getting into difficulty. I think we know a little more about the alkaline and the problems that we can have with it than we do with the lithium

and I want to emphasize again that I don't think we're overtesting. We had one system that we ran through these various tests, nine units, and everything went smoothly. We tested the unit off Ft. Lauderdale and during the air drop it was subsequently recovered and the battery let go violently and the system was able to sustain it. As it turned out on post mortum it was an internal cell short that you can't protect against and there are going to be manufacturing variances and we don't know what all tolerances are; however, how much water can you stick in here and get away with? We don't know what all the tolerances are and until we have that kind of handle I don't see that coming down the pike too soon.

The reason I brought it up was it is the real world and if we're going to use them we have to learn to deal with them and that's why the systems approach. Assume the worst is going to happen and we have a problem. In the fleet with Sonabouy, for example, these things get used, abused, dropped, etc. What are they supposed to do with them? Well they are grinding their way into the flashlights after they tear them apart with axes and things like that and that's the real world and we're going to have one go up sooner or later with that kind of abuse.

- Q. Taylor, Duracell: The real point that Frank made early in his talk, and it may have been missed, is do you need a lithium system? If the needs and wants exist and the expenditures to address the engineering at the power systems, battery module and cell level and do extensive testing, then yes, they can be safely employed.
- A. Marincic, Battery Engineering: I'd like to say a little more than that in my concluding remarks here. The answer is a qualified yes. We already have safe lithium systems. We are already making safe lithium batteries but we are taking too much risk by putting them into all kinds of applications where they don't belong. We don't have a universal lithium battery that can be used any way we need electrical power, and that is where we have to be more careful in choosing batteries and in choosing the application for them. I gave you, very quickly this morning, a few examples; I wish I had a whole morning to myself to tie you to your chairs so I could talk to

you about the details of that particular incident I investigated a year ago. I just couldn't believe what people are capable of doing and I'll describe it briefly to you. A very inferior design of the battery may be the old technology with the cheapest you can imagine and then for it to be placed into the most sensitive application you can imagine, other than the implantable, and if they had to "add" something ... This is the point that I missed this morning because I was rushed through my talk.

Somebody mentioned shock sensitivity this afternoon. I wanted to emphasize something that you may have missed but I don't know if I should mention it or not. In that accident there were 28 D cells. All 28 of them blew up in succession one after another in a closed system. There is a very big problem of shock sensitivity if you are keeping your batteries in a closed system and of course if you are using the wrong kinds of batteries. From the design in which I had collected 24 pieces from on the floor and assembled them. (I have slides but we do not have time for that), I could find only four out of the 28 glass seals. Shock sensitivity is the only way I could explain the explosions of 28 of them. Incidentally, when the battery blew up there was a basket of unused batteries from some bench sitting one foot away from that and none of those blew up; only those with enclosed systems. So, yes, we have a safe battery, no we don't have one. We had ignorant users, pardon the expression. I don't think anyone of you here count. You can always find them outside. How safe do you want it?

I can't tell you what IU has done in the last year. I have designed a battery and put it to 140 centigrades where it works for one full week delivering 160 milliamperes and then coming out and disassembling safely. You can design safe batteries, but you have to purify your electrolyte in case of thionyl-chloride and to make it totally hermetic you have to use stainless steel, not cobalt steel, and you have to make a tight, tight, structure inside. If you know how to do one of those you can eliminate probably 80% of the accidents that are happening these days with thionyl-chloride systems. So, did I make myself clear?

COMMENT

McDermott, Coppin State College: The part two graph that I showed was a result of coefficients generating from eagle-pic 55 ampere hour cells.

Q. Koehler, Ford Aerospace: Which parameters are most sensitive to charges on cell design?

A. Hafen, Lockheed: We really can't make a determination on that. Some difference rates involved in this particular test are due to the way it was set up. Variations and the depth of discharge also was a variation in the charges and discharge rate but we haven't spent enough time with the 35% and 20% DOD cells in order to work this out.

COMMENT

Halpert, GSFC: It was a constant current charge with taper at the end.

Q. Ebnor, Honeywell: Have you done any correlating of your models to actual experimental data?

A. Ernst, Naval Surface Weapons Center: We are not yet working with GT on the contract and they are going to instrument a test picture for us and we're going to do that. Just recently we started working on the code six through seven and it has taken time to get used to it and so forth but no, we're planning to do that. In fact, the program we're setting up to do that will probably do that very extensively.

Q. Halpert, GSFC: How big a part does that inductor play? I've seen cases where the inductor is really part of the electronics that you're using, circuit measuring and not part of the cell, and I'm not really sure how big a part that inductor plays?

A. Robin : That inductor indeed is a very intriguing one to bottle down and being new in the game of electrochemistry, it took me a long time before I decided it was an inductor and not some funny electrochemical reaction. One of the things we found was that your test wires resonate around one kilowatt, and unless you are very careful you'd think it's electrochemistry and not true inductors. So we went through building a so called coaxial structure which doesn't have any induction and we can't make that quite perfect.

- Q. Halpert, GSFC: Don is your model an academic exercise or is someone going to use it?
- A. Ernst, NSWC: I hope it's more than an academic exercise. Pat made two good points I'd like to elaborate on them. Mr. Nay has the magnesium silver-chloride seawater battery and the lithium-chloride battery and the aluminum silver-oxide battery and I doubt if anyone has used these programs for anything else but those exercises, particularly the magnesium silver-chloride battery. The model was very good and we got 5% accuracy but it was written specifically for the magnesium seawater battery. Part of the purpose of our work is to get a program that will handle any battery system or design that you want. The only thing you would have to change is the model that you draw and then put in the proper physical property data. The other thing in relation to that is there is a lack of data base for where you get this quantity of thionyl chloride at 60 degree C for example. Now Dr. Spock out at Naval Ocean System Center has tackled that part of the problem by having contracts written to determined physical properties.
- Q. Halpert, GSFC: I want to ask Mr. Robin, since he's done a lot of work of modeling electronic components, a question on one of the concerns that we have in modeling whole power systems. There are those who feel as though the battery may not be as important to the overall modeling of the power system as others feel it is. I am putting you on the spot by asking you this, but how do you feel about the modeling of the power system, or the importance of the battery in terms of modeling the overall power system and its components.
- A. Robin, co-author: Okay, that's the very point where we started looking at batteries coming from an electronics camp and we had the techniques available for solving all kinds of complicated electronic circuits but just specifying the modes of the components. It's a big book and you just go and ask for transistors, diodes, resistors, whatever and it may not become the available electrochemical camps. So these are very complicated

circuit diagrams when they are sketched out. They are easy to handle analytically and as such it just becomes a small part of a big complicated integrated circuit, so you're just tapping into that. One of the reasons we got going on this is that the battery provides you with a very good capacitor, that is the coupling element compared to the electrolytical capacitor. The only thing that is wrong with the battery is it does not match the requirements people come with. If we had made our electronics at 1.25 volts or 2.5 volts instead of 5 volts, for example, which is common at the present time for digital computers, everything would fit right in with the battery and the next scale probably would end up at 2.12 volts, so it matches.

So the dynamic properties of the battery make a terrific capacitor, probably better than anything else. The only thing is the voltage has to be about right, so you have to tell the other guy to use voltage capacitor for the electrochemistry. So up to, say 60 hertz, the coupling using analytic capacitor does a terrific job, better than anything else you can put your hands on and the only limitation is the endoctrion that probably related the physical size and since they are small you get a terrifically small endoctrion. When it comes to these long term things I believe a lot of the curve and measurements you call way out of deep discharge things, unless you very carefully specify the procedure by which you go through; I think you're going through loading up the grain inside. It's just a feeling that you have to be very precise how to define what the heck is going on. All you can say is that it sort of slowly settles down. Now we haven't gone too deeply into that, but that's true battery behavior. It's very slow, it takes hours, or so it seems like that. Does that answer your question?

COMMENT

Halpert, GSFC: When Ira was talking I remembered a dream three years ago where I started seeing grain sizes growing and so on and I wanted to do statistical modeling of that and I did this sort of thing which I think is very important. How you share the cell, how you grow grain boundaries and the interface between the conducting surfaces and active material is very important and I think we're just scratching the surface on that.

Bell Labs Representative: Can you comment on general availability and what your advise is to the outside world?

- A. Unidentified: Ira you looked into this and the advice is Bell Labs specifically. But there is a general computer program called Spice that is available all over the place and Ira may be able to tell you about it.
- A. Moskowitz, Bell Labs: Yeah, it's based on a computer program called Spice which is available and I think it started at Berkely; it was written there. And it was transported to Bell Labs then revised somewhat. Spice does everything that Advice does, and that is just one commonly available, and that's just one computer program there are many, many other computer programs similar to Advice with different powers. So the way to run this is to really get Spice, that's the most common one. But you get many other different versions.

COMMENT

Lackner, Canadian Defense: I think there is a point of interest here on an adequate data base. We're making a slight error in trying to understand the battery from modeling rather than from designing it for chemistry to design batteries for a variety of applications. The loading of the grains and the batteries is well known. If you have slightly loaded plates you are going to get a lot of current, and you possibly will stress the structure.

Now you can't understand any battery system from the outside so you cannot take a battery which Ira referred us to, as a living being it keeps changing its character whether you use it or you don't. If it's discharged and it sits on a shelf it's going to be different a year later; if it's charged and sits on a shelf--it's going to be different again. If you're cycling it, it'll be different. It's not an allowed electronic component but you can design it to operate along the paths you want for the manufacturer. So, I think we should try to be more careful not to look on it as an electronic component works by analyzing it to death, modeling it to death, and testing it to death.

COMMENT

Scott, TRW: This is in response to your comments on the data, of the two general approaches that were part of the question of this session.

I think a number of crunching machines necessary to implement that approach are available. All we need are the numbers and of course that's the big issue. Where are the numbers going to be coming from? And I agree with you, that that is probably the tougher part of the problem of modeling - setting good data to support a good model. That leads me to my second philosophical question if I may, and that is should we be putting the effort into a lot of modeling before we have adequate data that everybody recognizes is worth bothering with in the first place? If we do not then all we are doing is modeling individual tests there we will never know whether that model will indeed be general enough until we have almost all the data we need in the first place.

COMMENT

Robin: I'd like to comment on the interaction model and the data. I don't think it's a difference between theoretical and experimental physics. The two camps don't talk to each other. On the other hand, without having some sort of model you really don't know what to do and measure. And in some cases you don't have enough sensitivity to whether or not the particular measurements you're making on a given moment make any sense (for example, these past history effects that go into a particular experiment in a given moment). The battery is a living thing, indeed we have observed that, but it seems to me without having an intellectual vehicle upon which you can hang your sorts, you don't quite know what to go and measure or know what to pay attention to. And also, I believe that given the small micro-computers that we have available right now to control lab experiments, you basically set up your lab experiments and walk away. I'm not sure the effort is that enormous from this time on. In the past it was impossible and I couldn't agree with you more.

COMMENT

Moskowitz, Bell Labs: I don't think we can really afford the luxury of waiting to get all the data before we can start modeling. I think some of the Navy's experience with modeling, especially magnesium silver chloride battery, gave some really remarkable results and made it easier to develop it. They didn't have all the data, they didn't have all the complexities that are involved in the vinyl chloride battery either. I think one of the things we're trying to do is to get a model that we could use from one battery system to another, so the next time we come up with a new battery development we can use the same computer model, that hasn't been done before, but I don't think you can wait.

COMMENT

Kushner, Affiliation Unavailable: I wanted to comment that one of the functions of model simulation tool is that you have some confidence in it to tell you when you see something going on in an experimentry test; what data it is you need to go obtain in terms of physical characteristics. If you have a model that seems, to a reasonable extent, to represent the physics, chemistry, etc. of what's going on and you have seen some phenomena taking place that you can't explain, then by going through your model changing parameters, looking at variations in properties and things like some other phenomenon, you can at least see whether such occurrences or experiment. It can also save you from going down a lot of dead ends in that is showing up unaccountably on a test.

COMMENT

Scott, TRW: I'd like to comment also on that. Having sat through the accelerated test programs for a couple of years, I found that we became overwhelmed with just the data base itself. If we had it to do all over again, we would have tried to do some modeling at the beginning to figure out which data we should preprocess as we were going along, so that the data management thing becomes a lot more manageable. I think though that it's an interactive process until you sort of leap in and start doing the modeling, you don't know what data to ask for and it readily becomes a relationship of experiments. The theoretician is trying to nail it down and to optimize that relationship so that experimenters don't overwhelm you with thousands of magnetic tapes. I computed one time that if you put the data cards together from an accelerated test program it would go to the moon and back about three times or something.

COMMENT

Halpert, GSFC: This is the point where I usually throw my ax against manufacturers who unfortunately change processes and materials as we go along. It's unfortunate, of course, that we do a tremendous amount of work on one particular design and get a model, or at least some equations defining a voltage curve that Pat has spent quite a bit of time with and other people as well, and find like the plates have been changed.

We've been fighting this battery for a number of years. We finally had a standard cell, now we don't have a separator for that standard cell and we also have a change in a plate process. So we need to find some way in which we can model, not only the voltage characteristics of a cell, but also the property, the physical property, which is tough.

COMMENT

Thierfelder, General Electric: I just wanted to comment on one of Gerry's earlier comments about the effect of the battery at the GE Space Center. We have computer models of practically all of our power subsystems, and we've gotten to the point where we do each one individually because each power subsystem, the solar array, and the other components and the way they put together the battery. One other comment: all this data is actually empirical data and the battery data that we get from actual tests on those batteries is, that subsystems are used in that computer model. So it's all empirical and we've gotten to the point of doing each one as an individual computer model.

Q. Scott, TRW: Does the battery act the same when you put a new power charge configuration on it and so on?

A. Thierfelder, General Electric: We are using actual test data for those batteries and since our latest computer program has the batteries data from that program in it they are just modeling the curve that we've gotten in the tests.

Q. Scott, TRW: Well, it's not really a problem. I mean it's going out in a year.

A. Thierfelder, General Electric: Well, we have this out for ten years. One of the outputs of the computer program is to predict what that system will do in ten years, and our batteries are not to be deflagrated. That's one of the assumptions.

Q. Robin: To me it's interesting to hear how these GE batteries are modeled. I guess you saw we've been measuring some of your batteries. And coming again as an electronic engineer I look at all these catalogs and I see all those curves and I am lost. It takes a computer to figure out what the heck it is. One of the ways I got going looking at the battery circuit elements is by using

components the electronic engineer is familiar with you can get a pretty good hang of what will happen when you put it into a circuit. More or less by inspection you look at this circuit diagram Ira put on the screen and you know what will happen. You don't need to do any further computer analysis from the point of view of general features and general behavior. It's a very nice and potent vehicle, it doesn't take a computer to figure out what's going on. So if you condense your data into that format you can communicate it to an electronic engineer.

SESSION II

"MODELLING - IS THE EMPIRICAL OR SCIENTIFIC BASIS MORE
RELIABLE AND USEFUL FOR PRIMARY AND SECONDARY CELLS?"

P. McDermott, Chairman
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MODELING - IS THE EMPIRICAL OR SCIENTIFIC BASIS MORE RELIABLE AND USEFUL FOR PRIMARY AND SECONDARY CELLS?

Introduction

Patrick P. McDermott

When one reads the title of our session, the impression is given that we will have a contest between two different modeling philosophies. At the end of the session we will have a show of hands and declare a winner. Not likely! The idea, however, is to contrast these two different approaches to modeling and other approaches which might be characterized as semi-empirical.

We may quibble about the use of the word empirical as contrasted to scientific, but what we mean to define here is two approaches to modeling which emphasize different aspects or start from different premises. By scientific, we mean a model which starts with or emphasizes the electrochemistry of the battery. What are the laws which govern its operation e.g., diffusion thermodynamics, use of the Nerst equation to predict voltage, etc.

At the other extreme, the empirical approach battery is considered as a black box. If treated in a certain way, one will observe a certain response. There is little concern about the chemical reactions taking place inside the battery.

What is modeling? Let us not quibble about terminology, but accept a rather broad definition. Anything which simulates cell behavior, which predicts how a cell will operate given a certain environment, which relates the laws of physics and chemistry to cell operation, life, reliability, would fit our definition. The unifying theme throughout the session is the question of utility. Is the model useful? How does it help me?

Models can be useful for a number of reasons, but the emphasis should be on practicality. Does it, for example,

- o Help me understand how long the battery will last in orbit?
- o Help me predict what the voltage will be during a particular period in its life so that I will be able to coordinate my power management?
- o Help me contribute information for larger power systems models where the battery become a subcomponent of a larger system?
- o Help me understand the internal workings of the cell so I can design a better battery?

Does the model finally help me understand the basic physics and chemistry of cell operation? Knowledge for the sake of knowledge.

We really can't make long term improvements in batteries if we don't know how it works.

We can see there are very many motivations for doing cell modeling and I think we will see more of it as time goes on. One major driver is the availability of microcomputers and software so that the individual can make progress without having to cue up to the big computer.

We have a good range of papers today which cover the spectrum. The first I would characterize as very empirical, the second as semi-empirical, and the third as basically a scientific model. All three are operationally oriented in that they are aimed at predicting voltage during charge and discharge for secondary cells. The fourth paper will be of interest to the Lithium people and is oriented toward optimizing cell design.

We do have additional papers which are not on the program, but are welcomed additions to our discussion today. One is a computer model of battery behavior using the concept of non-linear circuit elements as on equivalent circuits to be presented by scientists from Bell Laboratories. Another paper by Y. Dubois, MATRA Space Center, Toulouse, France, will not be presented in this session, but will be included in the proceedings.

BATTERY MODEL
FOR ELECTRICAL POWER SYSTEM
ENERGY BALANCE

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Abstract

A model to simulate nickel-cadmium battery performance and response in a spacecraft electrical power system energy balance calculation has been developed. The voltage of the battery is given as a function of temperature, operating depth-of-charge (DOD), and battery state-of-charge. Also accounted for is charge inefficiency. A battery is modeled by analysis of the results of a multiparameter battery cycling test at various temperatures and DOD's.

Introduction

A model developed to simulate nickel-cadmium battery performance and response characteristics has been integrated into a computer program which simulates the behavior of a multi-battery/solar array spacecraft electrical power system.

The battery model is derived from laboratory battery cycling data. "Steady-state" charge/discharge voltage vs. time data is first generated for each of a number of temperatures and operating DOD's. The voltage-time data is then transformed to voltage vs. capacity data assuming derived cycle charge efficiencies. Coefficients are then best fit for cubic equations for the charge curves and the discharge curves for each of the temperature and DOD conditions of the testing. Once this is accomplished, constants are derived which will predict the above coefficients as a function of temperature and operating DOD. Voltage variation for various charge and discharge rates is determined using constant impedance lines which intersect the baseline charge or discharge voltage corresponding to currents at the operating DOD.

Description of Model

For a given battery type, the battery model constructs a battery voltage-current relationship as a function of three variables: temperature, operating DOD and battery state-of-charge. The battery response is characterized by an ensemble of voltages corresponding to a set of currents, producing an "I-V" curve for the battery at that particular point in time. The dependence of battery voltage on operating DOD stems from the fact that discharge current depends on the DOD for a constant discharge time. Discharge current affects, for example, the recombination rate, oxygen pressure, and cell internal temperature. The process of synthesizing this curve is represented in Figure 1. Initially, an equation is developed for baseline charge and discharge voltage vs. state of charge. These baseline voltages corresponds to baseline currents which would produce the operating DOD given the charge or discharge time. The baseline currents are calculated as follows:

Baseline Charge Current:

$$i_{CO} = \frac{(\text{DOD}) (\text{Maximum recharge ratio}) (\text{Battery capacity})}{(\text{Total charge time})}$$

Baseline Discharge Current:

$$i_{DO} = \frac{(\text{DOD}) (\text{Battery capacity})}{(\text{Discharge time})}$$

Note that charge current is negative while discharge current is positive.

The next step in constructing the voltage-current curve is to calculate a single baseline charge and discharge voltage for the battery's present state-of-charge. Finally, the full voltage-current curve is developed. For values of current close to the baseline currents, the voltage-current relationships are assumed to be linear, with a slope equal to battery impedance. That is, for each current close to the baseline current, voltage is calculated as the following:

Charge Currents:

$$V_C = V_{CO} - Z(i - i_{CO})$$

Discharge Currents:

$$V_D = V_{DO} - Z(i - i_{DO})$$

In the region close to zero current, the voltages are calculated according to a cubic function of current so that voltage and slopes are matched at the transition points between the cubic function and straightline regions.

Model Application

For a given battery, a model is developed by analysis of the results of a multi-parameter battery cell cycling test. More than one cell design can be used to generate the model coefficients if the cells are fairly close in design (i.e. comparable precharge ratios and loading levels). The multiparameter cycling test is a test in which cells are electrically cycled over a matrix of temperatures, DOD's and charge voltage cutoffs. Typical cycle test times are 35 minutes for discharge and 55 minutes for charge. The main charge is in effect until the voltage cutoff is reached; trickle charge is in effect for the remainder of the 55 minutes. Main charge, trickle charge, and discharge are constant current. Cycling continues until stabilization occurs; adjacent cycles having equal charge times with no voltage degradation. After stabilization, voltage vs. time data is recorded.

The multiparameter test data is used to generate model coefficients as shown in Figure 2. Only the test data using the highest charge voltage cutoff is used for each point in the temperature/DOD matrix, with end-of-charge corresponding to full state-of-charge. The co-efficient development calls for taking N battery cell voltage curves, having one charge/discharge cycle each, to produce forty model coefficients (twenty for charge, twenty for discharge). The first part of the modeling procedure is to fit voltage during each charge or discharge to a cubic with state-of-charge as the independent variable. This results in eight co-efficients for each parametric test condition (four for charge, four for discharge). A cubic was chosen to model the curve since it successfully modelled the voltage, and the fact that fitting higher ordered equations required operating with a near-zero matrix (i.e., ill-conditioned problem). For each of the eight co-efficients, the corresponding co-efficients from the N parameter tests are used to obtain the coefficient as a function of temperature and DOD. Thus all eight cubic co-efficients are defined by such a function. The dependence of the eight co-efficients on temperature and DOD may be determined algebraically if only five combinations of temperature and DOD are available.

Model Characteristics

A battery model has been developed for beginning-of-life Eagle-Picher RNS 55-3 hardware. The behavior of this model is discussed below. The battery voltage at full charge is depicted in Figure 3 as a function of temperature. Operating DOD has a small effect on the full charge voltage. A comparison of the battery

charge voltage curve with a typical charge control cutoff curve is also shown. Minimum discharge voltage for the RSN 55-3 model is shown in Figure 4. The voltage is shown at a state-of-charge equal to one minus the operating DOD. It was also validated that cell voltage is a strictly increasing function of state-of-charge for the ranges of operating DOD and temperature modelled.

Model Utilization

A computer program was developed which utilizes this battery model to simulate a multi-battery/solar array electrical power system. The program models the power system as a number of power source sub-sections, each connected to a common bus through a resistor/diode combination. Each of the sub-sections contains a battery, charge control unit and associated array module or modules. Either bi-level relay switching or PWM charge control units may be modeled.

The program computes an energy balance between all components of the vehicle power system at set intervals around the vehicle orbit. The energy balance is computed using a matrix solution of piecewise linearized voltage node equations in an iterative process.

$$a_i(T, DOD) = C_{i,1} (DOD)^2 + C_{i,2} (DOD) + C_{i,3} + C_{i,4} (T-25) + C_{i,5} (T-25)^2$$

$$b_i(T, DOD) = d_{i,1} (DOD)^2 + d_{i,2} (DOD) + d_{i,3} + d_{i,4} (T-25) + d_{i,5} (T-25)^2$$

FOR $i=0, 1, 2, 3$

TEMPERATURE
DOD

EQUATIONS FOR BASELINE
CHARGE AND DISCHARGE
VOLTAGE AS FUNCTION OF
STATE OF CHARGE

$$V_{C0} = a_3 s^3 + a_2 s^2 + a_1 s + a_0$$

$$V_{D0} = b_3 s^3 + b_2 s^2 + b_1 s + b_0$$

NOTE: DISCHARGE CURRENT
IS POSITIVE
CHARGE CURRENT IS
NEGATIVE

BASELINE CHARGE CURRENT

$$i_{CO} = \frac{(DOD) (\text{MAX RECHARGE RATIO}) (\text{BATTERY CAP})}{(\text{TOTAL CHARGE TIME})}$$

BASELINE DISCHARGE CURRENT

$$i_{DO} = \frac{(DOD) (\text{BATTERY CAP})}{(\text{DISCHARGE TIME})}$$

STATE OF
CHARGE, s

VOLTAGE

CURRENT

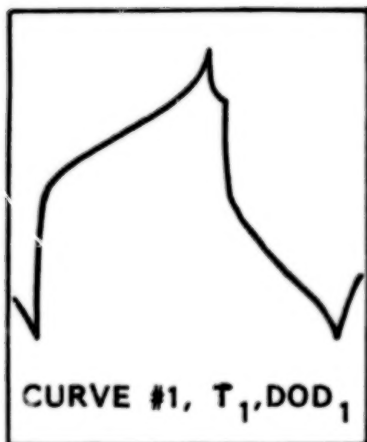
STRAIGHTLINE REGIONS
BASED ON IMPEDANCE

$$V_C = V_{C0} - Z(i - i_{CO})$$

$$V_D = V_{D0} - Z(i - i_{DO})$$

CUBIC FIT IN REGION CLOSE TO
ZERO CURRENT TO MATCH SLOPE
AND VOLTAGE IN CHARGE AND
DISCHARGE REGIONS

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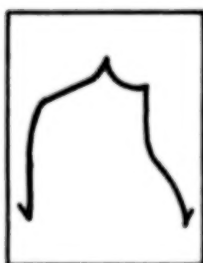
BEST FIT CUBIC FOR CHARGE:

$$V_c = a_{3,1}s^3 + a_{2,1}s^2 + a_{1,1}s + a_{0,1}$$

WHERE \bar{s} IS STATE OF CHARGE.

BEST FIT CUBIC FOR DISCHARGE:

$$V_d = b_{3,1}s^3 + b_{2,1}s^2 + b_{1,1}s + b_{0,1}$$



BEST FIT CUBICS FOR T_2, DOD_2 .



BEST FIT CUBICS FOR T_N, DOD_N .

FIT a_3, a_2, a_1, a_0

b_3, b_2, b_1, b_0

TO EQUATIONS AS
FUNCTION OF T, DOD

e.g.

$$a_i(T, DOD) = c_{i,1}(DOD)^2 + c_{i,2}(DOD)$$

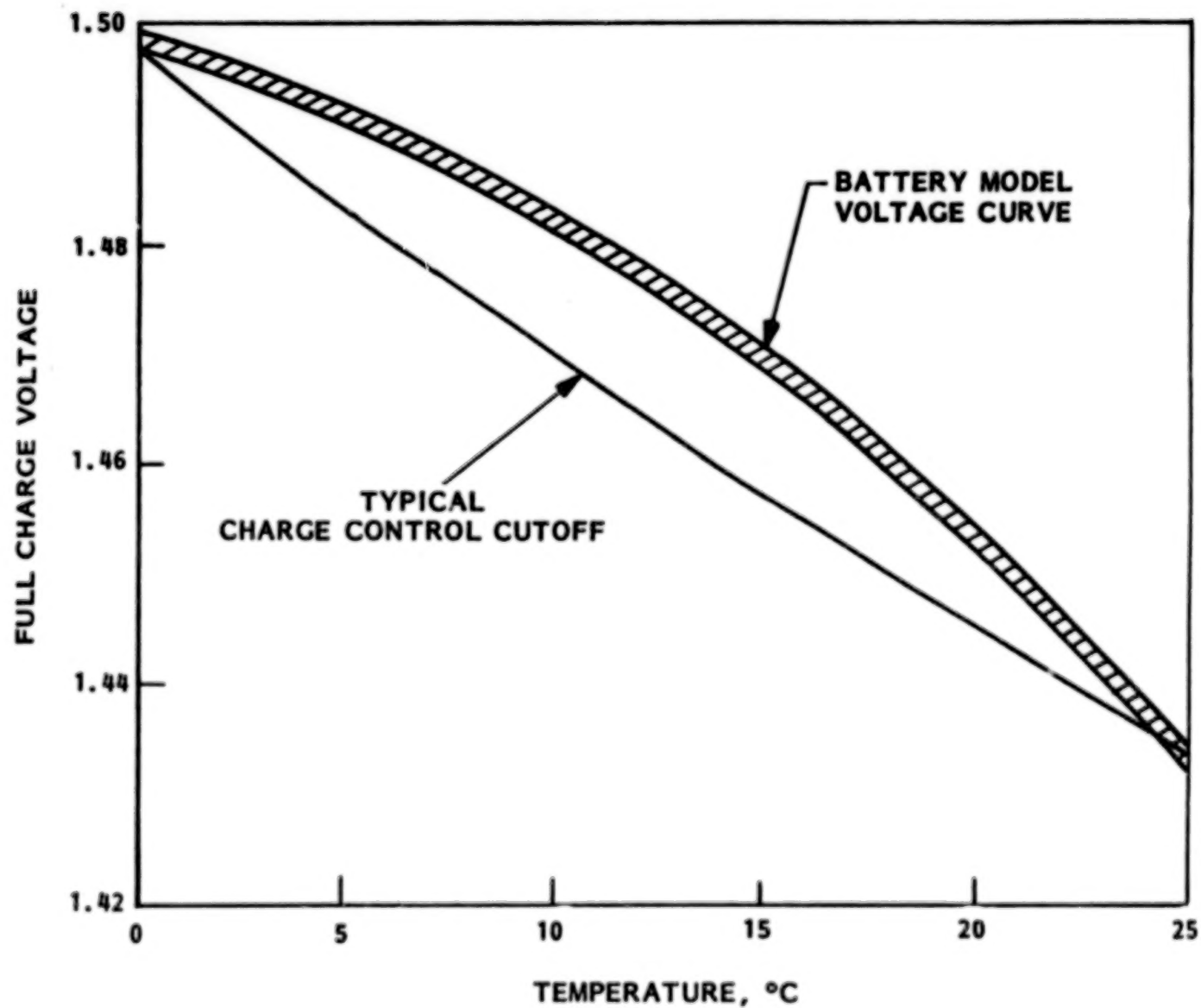
$$+ c_{i,3} + c_{i,4}(T-25) + c_{i,5}(T-25)^2$$

$$b_i(T, DOD) = d_{i,1}(DOD)^2 + d_{i,2}(DOD)$$

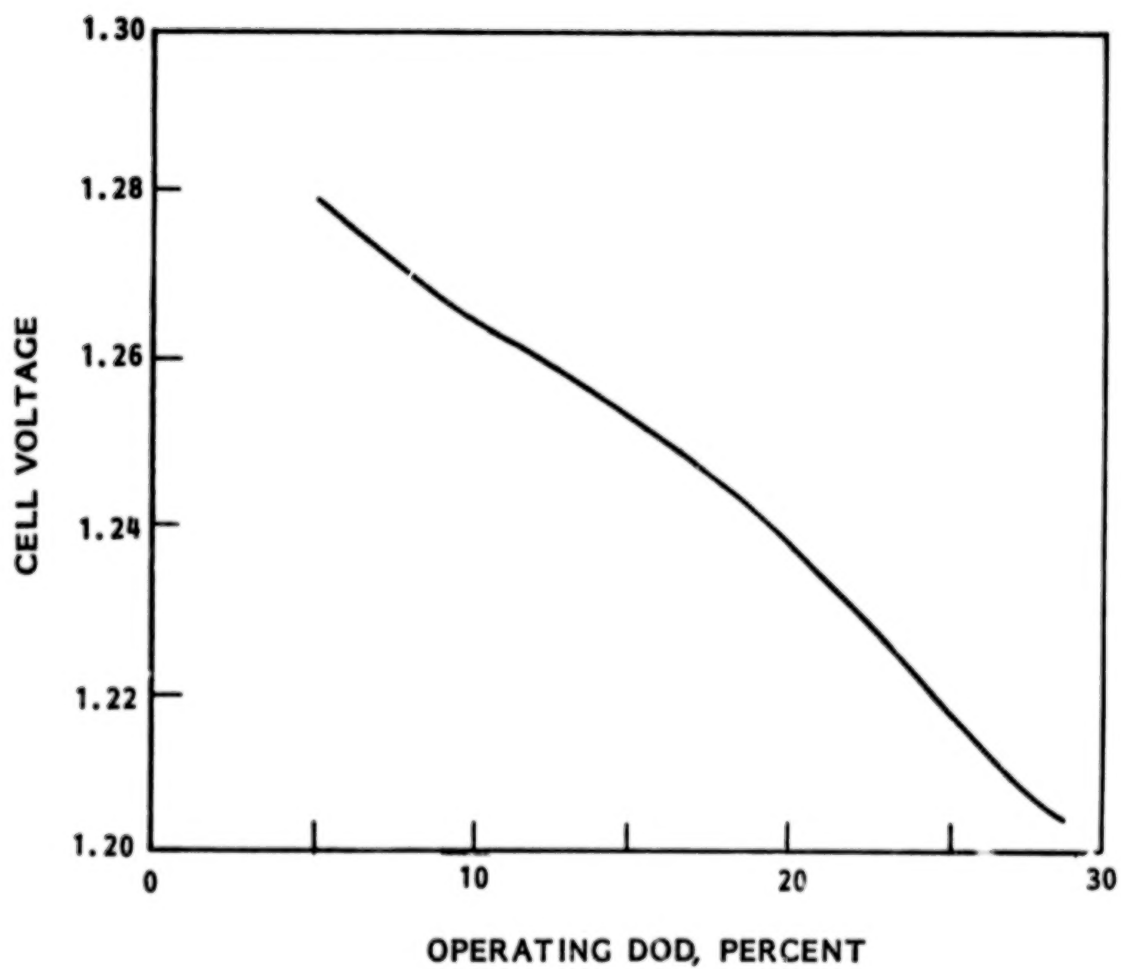
$$+ d_{i,3} + d_{i,4}(T-25) + d_{i,5}(T-25)^2$$

FOR $i=0, 1, 2, 3$

FIGURE 3. BATTERY MODEL FULL CHARGE VOLTAGE DoD = 15 - 30%



**FIGURE 4. MINIMUM DISCHARGE VOLTAGE
STATE-OF-CHARGE CORRESPONDS TO
OPERATING DOD**



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**MODELING BATTERY LIFE THROUGH
CHANGES IN VOLTAGE FIT COEFFICIENTS**

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Introduction

This paper discusses a program which has been in progress for some time and which was the subject of a presentation at last year's Goddard Space Flight Center Battery Workshop. At that time, preliminary results were presented on analysis of battery discharge voltage using non-linear regression analysis of data from a test which was being conducted at the Jet Propulsion Laboratory. In this test, a number of 12 ampere-hour cells, nickel cadmium, were being cycled under various conditions of temperature and depth of discharge (DOD). Using this data, it was confirmed that a five parameter fit equation could be used to model the JPL data within a few millivolts.

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Since that time, these studies have been extended, and literally hundreds of voltage curves, both charge and discharge, have been examined to discover the impact of factors such as temperature and DOD on the fit coefficients. These studies have led to some interesting observations concerning the aging of nickel cadmium cells as they age. There are definite patterns or trends observed when the fit coefficients are plotted versus cycles.

Five Parameter Fit Equation

The five parameter equation for fitting the charge and discharge curves are shown below.

Discharge Voltage	=	A	-	$\frac{B}{C - x}$	+	De^{-Ex}
Charge Voltage	=	A	+	$\frac{B}{C - x}$	-	De^{-Ex}

The equations have identical terms and vary only in the algebraic signs in front of the second and third terms. The discharge curve has a negative sign in front of the second term and the charge curve has positive. Likewise, the last term has a positive sign for the discharge curve and a negative for the charge curve.

Essentially, the De^{-Ex} term relates to the exponential-like decline in voltage right at the beginning of discharge

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with the $B/(C-x)$ term taking care of the gradual falling off of the voltage during the latter stages of discharge.

In the case of charge, these effects are reversed. The De^{-Ex} term accounts for the sharp rise in voltage at the beginning of charge, and the other terms account for the more gradual rise in voltage as the charge progresses, culminating in the turn upward again in the voltage as the cell reaches the end of charge. The x in these equations refers to the ampere hours of current passing through the cell during the charge or discharge. The A , B , C , D , and E are the fit coefficients. Their value is determined by allowing the computer to fit the data using a non-linear regression software package. The computer was the Hewlett-Packard 9845.

Examples of Charge and Discharge Curve Fits

The first series of figures show the fits for various temperatures and DOD. In the first two, Figures 1(a) and 1(b), a dotted line has been added to indicate the effects of each of the fit coefficients. The dotted line represents, essentially, the effects of A , B , and C in the fit equation, as if the equation were plotted without the third term. The De^{-Ex} term therefore represents the difference between the solid line at the beginning of discharge and the dotted line.

Figure 1(b) shows the curve of a cell at the same

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conditions of DOD and numbers of cycles accumulated as Figure 1(a) but at an increased temperature, 30° C. This figure shows as did Figure 1(a) a very close fit of the computer calculated line with the dots which represent the actual data points. The line fits the data points within a few millivolts. Figure 1(c) shows similar conditions, but at 40° C. There is a sharper curvature toward the right side of the graph as the cell reaches the end of discharge.

The next series of figures, 2(a) through 2(c) show the same conditions of temperature and DOD at 2000 instead of 1000 cycles. The trends are very similar, but as the cell ages, there is more of a rounding off of the curve toward the right side as the cell reaches the end of discharge.

Figure 3 illustrates our interpretation of parameter C as an indicator of the capacity, or what might be called the apparent capacity of the cell under certain conditions. In the second term of our equation, $B/(C-x)$, as x approaches some value C, the denominator becomes smaller and smaller which means that the whole term becomes large. Since it is a negative term in the discharge fit equation, the effect will be to drive the voltage down as x approaches C. One could interpret this physically as the cell reaching the end of its capacity, at which point the voltage would drop. Eventhough the cell may have additional chemical capacity, the cell cycling at a particular DOD will "memorize" a certain routine. It will act as if it were running out of

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capacity. This is therefore designated as the apparent capacity which approaches parameter C as a limit.

The next series of figures, 4(a) through 4(f) show 35% DOD cells on charge at various temperatures at 200 and 3100 cycles. We have found that our equation will fit these curves, again almost perfectly, if the curves show a nice rounding off at both the beginning of the curve and at the upper right hand portion of the curve, as the voltage increases toward the end of the charge. One can gain an insight here as to why the charge curve can be fit with the same terms as the discharge curve, the only difference being the signs before the second and third terms. If these figures were inverted, they would have shapes very similar to shapes found in the discharge curves.

Almost all of the charge curves were almost perfect fits with the exception of Figure 4(c). A careful examination of the data points will show that they do not follow the regular sigmoid shape we are accustomed to fitting. The curve seems to taper off at the top, as one might expect, as the cell goes into overcharge. We have found that to fit the charge curve properly with our equation, we have had to stop inputting data points when the curve changes direction and tends toward a second plateau on charge. The equation in other words cannot negotiate another change of direction at the end of charge.

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Fit Parameters Versus Cycles for Charge and Discharge

The next series of figures shows the individual parameters A, B, C, D, and E of the fit equations plotted against cycles. The data points for the 50% DOD cells are given every one hundred cycles. For purposes of comparison, all five parameters versus cycles for the 50% DOD cell at 20° C are plotted together in Figure 5.

One notices immediately some distinctive characteristics. All of the parameters with the exception of parameter D experience a sharp rise in value for the first one hundred cycles and then show a gradual decline in value over the next thousand cycles up to approximately 1300 to 1500 cycles. At this point, the curves flatten out and become somewhat stable, reaching a sort of equilibrium. For parameter D, the trend is similar, except opposite in slope. The curve initially drops, then rises gradually to 1500 cycles, then flattens out.

Figure 6 shows the same set of conditions, but with the cells on charge instead of discharge. If Figures 5 and 6 are compared, significant differences are noted. First of all, there is not the initial rise or drop in voltage over the first hundred cycles. There is, however, the gradual trend downward over the first thousand cycles for parameters B, C, and E with a trend upward for A and D before all the curves level off. It is interesting to note that the charge curves level off sooner than the discharge curves, at around a thousand cycles versus 1300 to 1500 cycles. The other trends are

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similar except for parameter A where the gradual slope is down for discharge and up for charge.

Effects of Temperature on Fit Parameters

The effect of temperature is shown in Figures 7(a) through 7(e). Figure 7(a) is a comparison of parameter A at three temperatures, 20° C, 30° C, and 40° C. The same general pattern is recognized, the sharp initial rise, then a gradual slope downward before leveling off, except here one observes the major effect of temperature. The leveling off occurs at earlier cycles for progressively higher temperatures, at around 800 cycles for 30° C and 500 cycles for 40° C. All of the curves level off at very near the same voltage, 1.29 volts.

Figure 7(b) shows parameter B for the same three cells. The same pattern observed at 20° C, the top curve, is reflected in the curves at 30° C and 40° C, except the leveling off occurs at progressively earlier cycles, this time at approximately 700 and 400 cycles respectively.

Figure 7(c) shows parameter C also leveling off at progressively earlier cycles. It is interesting to note here that all of the curves level off with an apparent capacity of 7 ampere hours. This is an illustration of the phenomenon where a cell cycling at a particular DOD will eventually "memorize" that level of discharge. This does not mean that the cell has only 7 ampere hours of capacity in an absolute sense, but rather that the voltage is dropping

on discharge as if the cell only had 7 ampere hours of discharge capacity. If the cell had been allowed to discharge further, the voltage curve would have flattened out to a second plateau for the duration of the discharge to zero volts.

Figure 7(d) shows the same pattern for parameter D except the gradual slope is upward with the leveling off occurring at progressively earlier cycles at the higher temperatures.

Parameter E shown in Figure 7(e) demonstrates the same trend.

Effects of Depth of Discharge on Fit Parameters

Figures 8, 9, and 10 show cells cycled at depths of discharge other than 50%. These figures have data points every 200 or 300 cycles instead of the 100 cycle intervals found in the 50% DOD figures. The patterns are, therefore, not as well established, but interesting differences are observed when these results are compared with those at the 50% DOD. In Figure 8, which is the 35% DOD discharge at 20° C, the same pattern is observed as before, with the gradual slope up to approximately 1300 to 1500 cycles, then the flattening out. It should be noted, however, that the slopes for parameters D and E are opposite from those found at 50% DOD.

The most unusual pattern was found at 20% DOD, Figure 9. Here only three of the parameters are displayed, but we see

that A, B, and C all show two plateaus, with a transition between approximately 1900 and 2500 cycles. The suspicion is that this cell was not being fully charged during the earlier cycles. Note that parameter C, the apparent capacity, is very low at the beginning, around 4.5 ampere hours at the beginning of life, and gradually works up to around 7.5 ampere hours toward the latter cycles. As was seen previously, A, B, and C seem to be acting in concert, that is, movement of one parameter is reflected in the others.

In Figure 10, parameters D and E for this 20% DOD cell have trends which are quite different from those seen previously. Although these results are interesting, time has not permitted an in depth analysis of the results similar to that performed on the data from the 50% DOD cells.

Correlations Among the Fit Parameters

Figures 11(a) through 11(c) show rather dramatically what was already suspected, that A, B, and C are strongly correlated. In Figure 11(a), parameter A versus C shows a very strong linear relationship as reflected in the line fitting the data points, $A = 1.072 + .03C$. Figure 11(b) shows the same relationship for the higher temperature 30° C. The line has the same slope, .03, but has a slightly different intercept, 1.068. Figure 11(c) demonstrates the same pattern at 40° C. The slope is the same, but the intercept

is slightly different, 1.066.

Based on the interrelationships among the parameters, a new fit equation has been developed which has only three parameters instead of the five.

$$\text{Discharge Voltage} = A_{\text{temp}} - \frac{(.17 - 0.8 C)^2}{C - x} + D e^{-Ex}$$

$$\begin{aligned} \text{Where } A_{\text{temp}} &= 1.072 + .03 C \text{ (20°)} \\ &1.068 + .03 C \text{ (30°)} \\ &1.066 + .03 C \text{ (40°)} \end{aligned}$$

In the equation, the original parameter A is replaced with A_{temp} where A_{temp} equals the three temperature dependent linear equations shown above and in Figures 11(a) through 11(c), all a function of C only. Using a similar methodology, we substituted another expression for old parameter B based on an observed parabolic relationship between B and C. This is the expression $(.17 - 0.8C)^2$ in the numerator of the second term. Now both A and B have been replaced by expressions which contain C only and some constants.

A number of curves have been fitted with this three parameter equation. Our experience has shown that this new equation will fit the data well, but with no where near the accuracy of the five parameter fit.

Conclusions

In summary, using the five parameter fit equation, both charge and discharge curves can be fit with accuracies

in the range of one or two millivolts. The fit coefficients when plotted versus cycles show definite trends and patterns which can be used in an operational sense to predict battery voltage as a function of temperature and DOD.

The calculation of parameter C is particularly important. It allows the operator to detect anomalies in battery behavior by examination of the voltage curves where very small changes in the voltage curves, too subtle for even the experienced eye, can be readily recorded as measurable changes in the fit parameter. Since voltage data can be readily telemetered to earth from the satellite, this allows for real time diagnostics of battery behavior.

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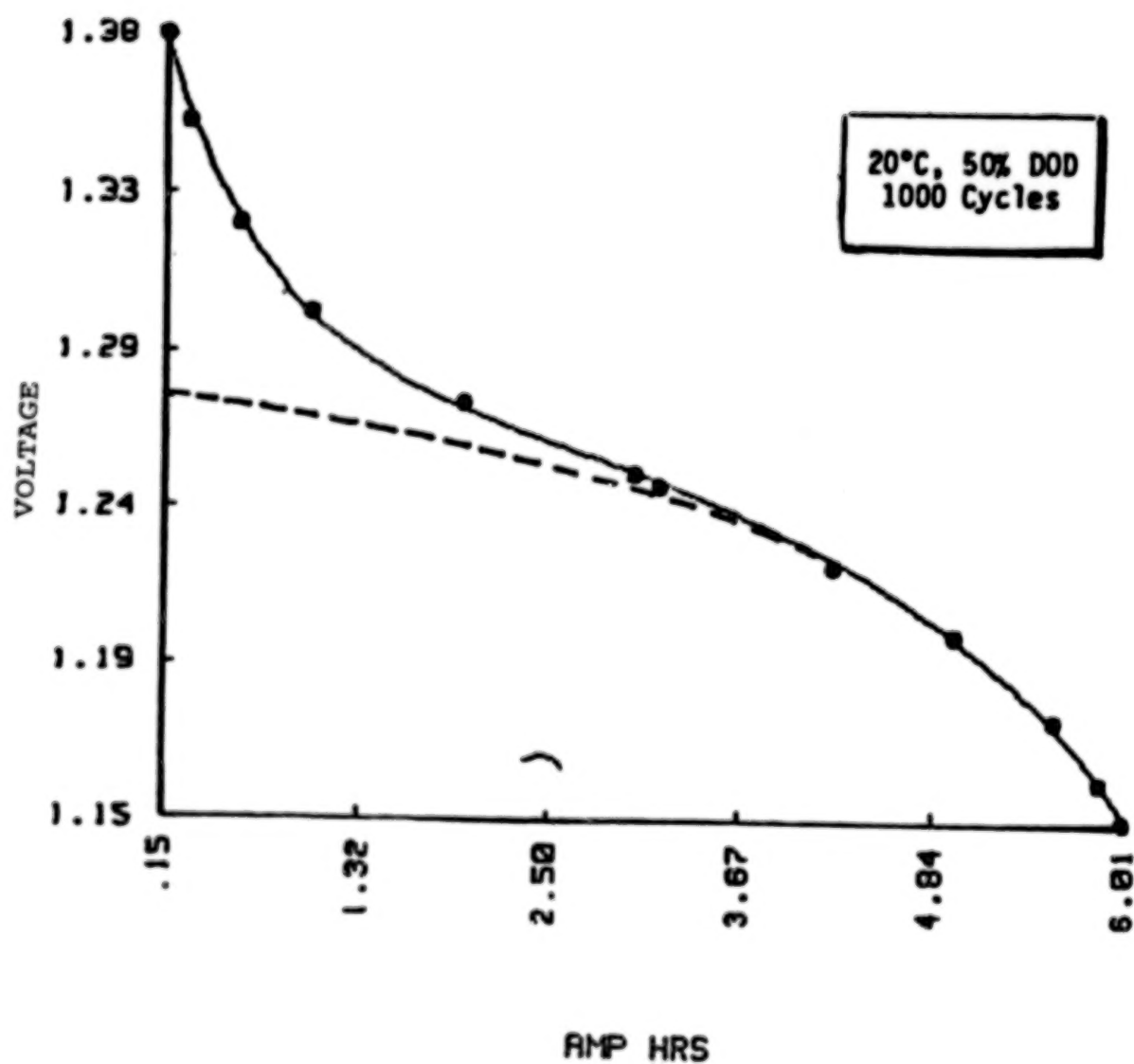


FIGURE 1(a) FIVE PARAMETER DISCHARGE VOLTAGE FIT

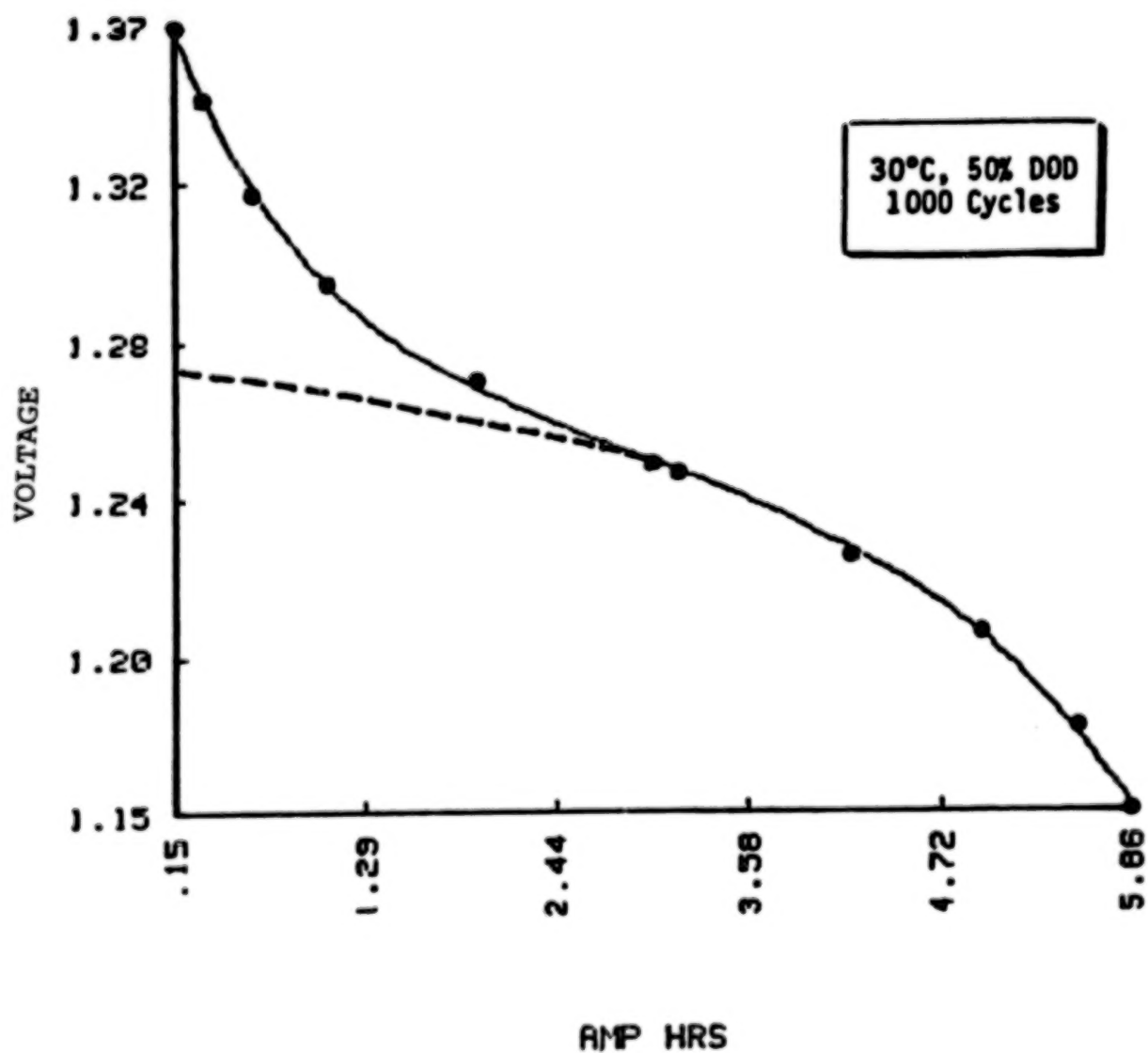


FIGURE 1(b) FIVE PARAMETER DISCHARGE VOLTAGE FIT

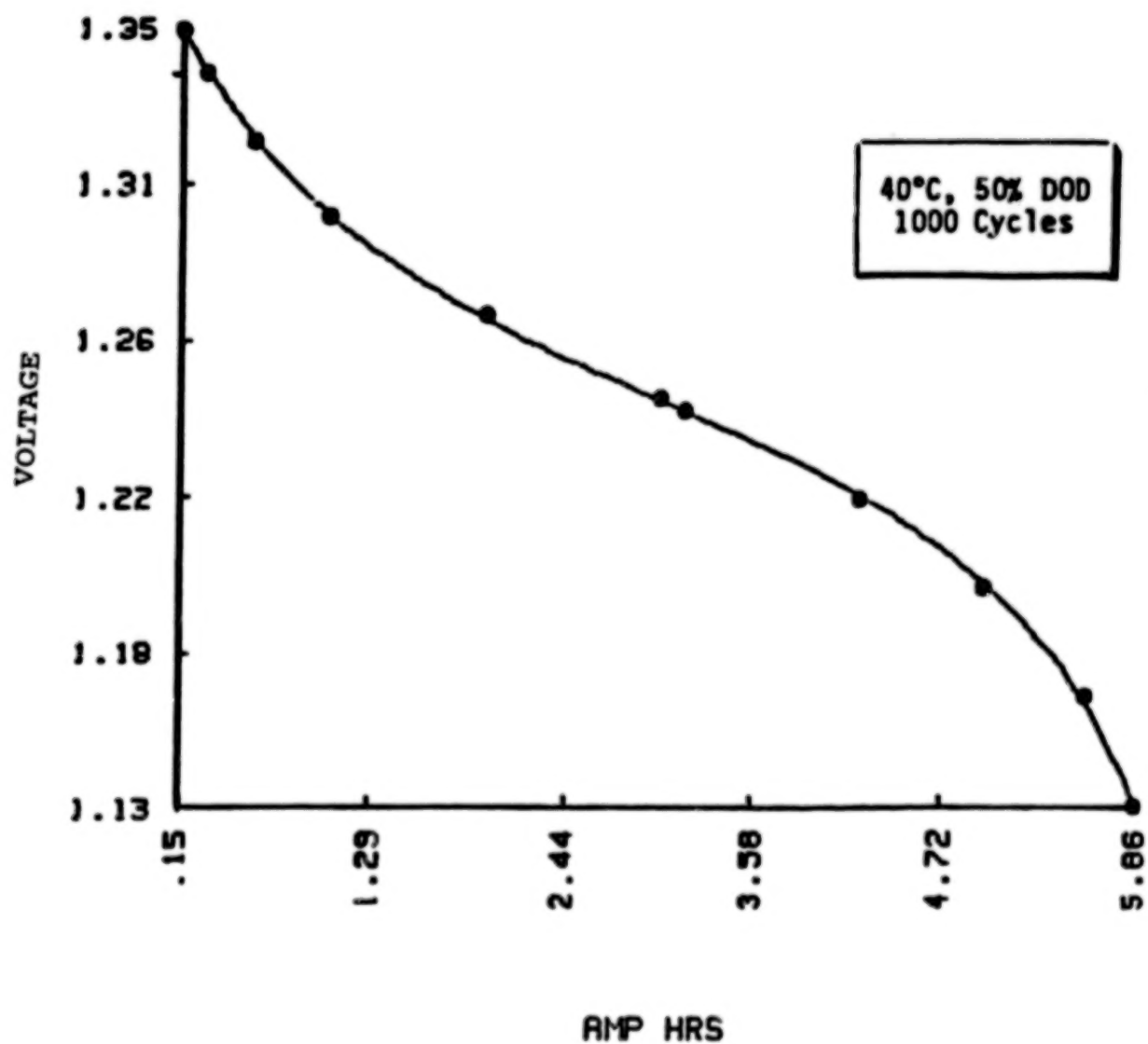


FIGURE 1(c) FIVE PARAMETER DISCHARGE VOLTAGE FIT

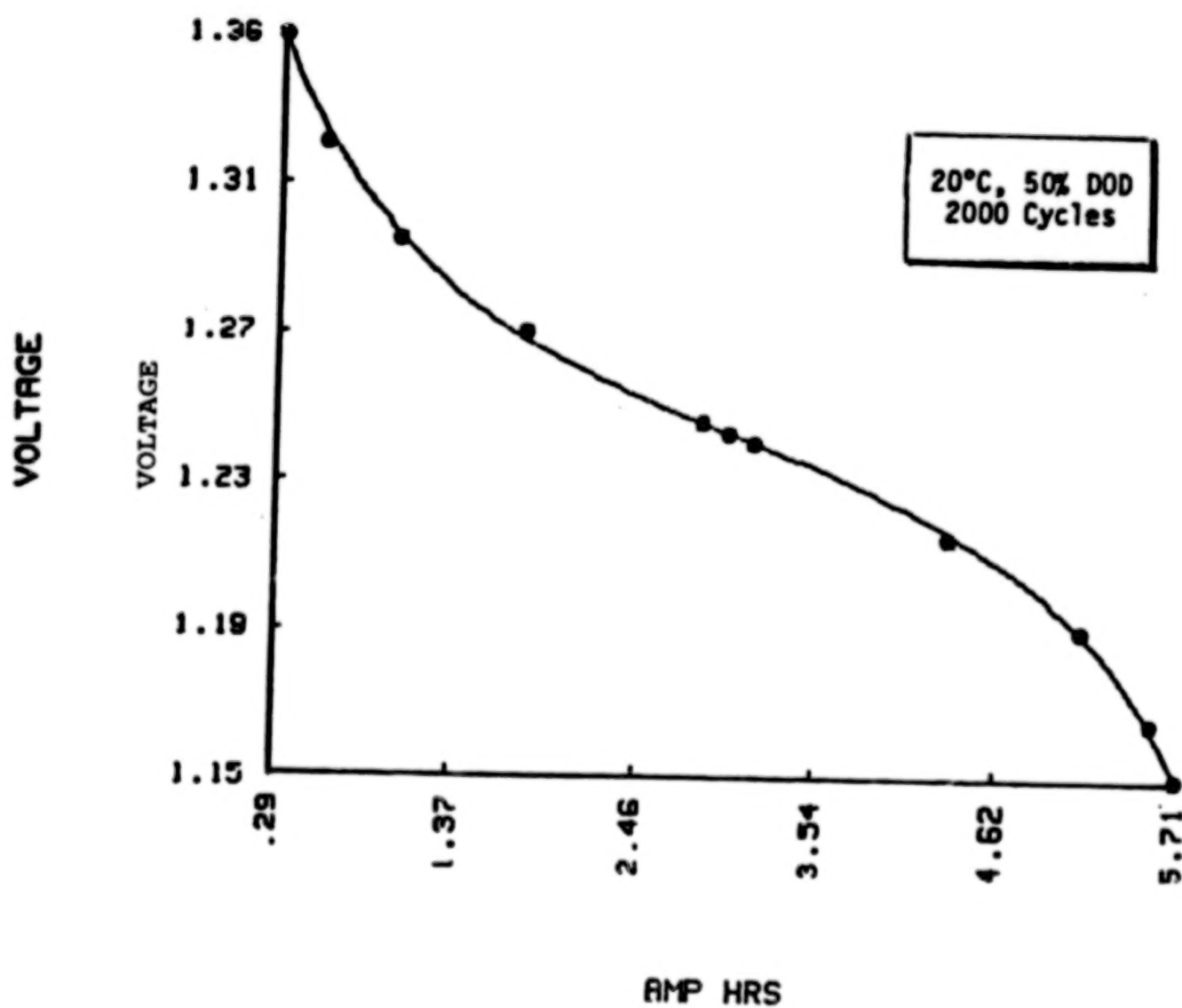


FIGURE 2(a) FIVE PARAMETER DISCHARGE VOLTAGE FIT

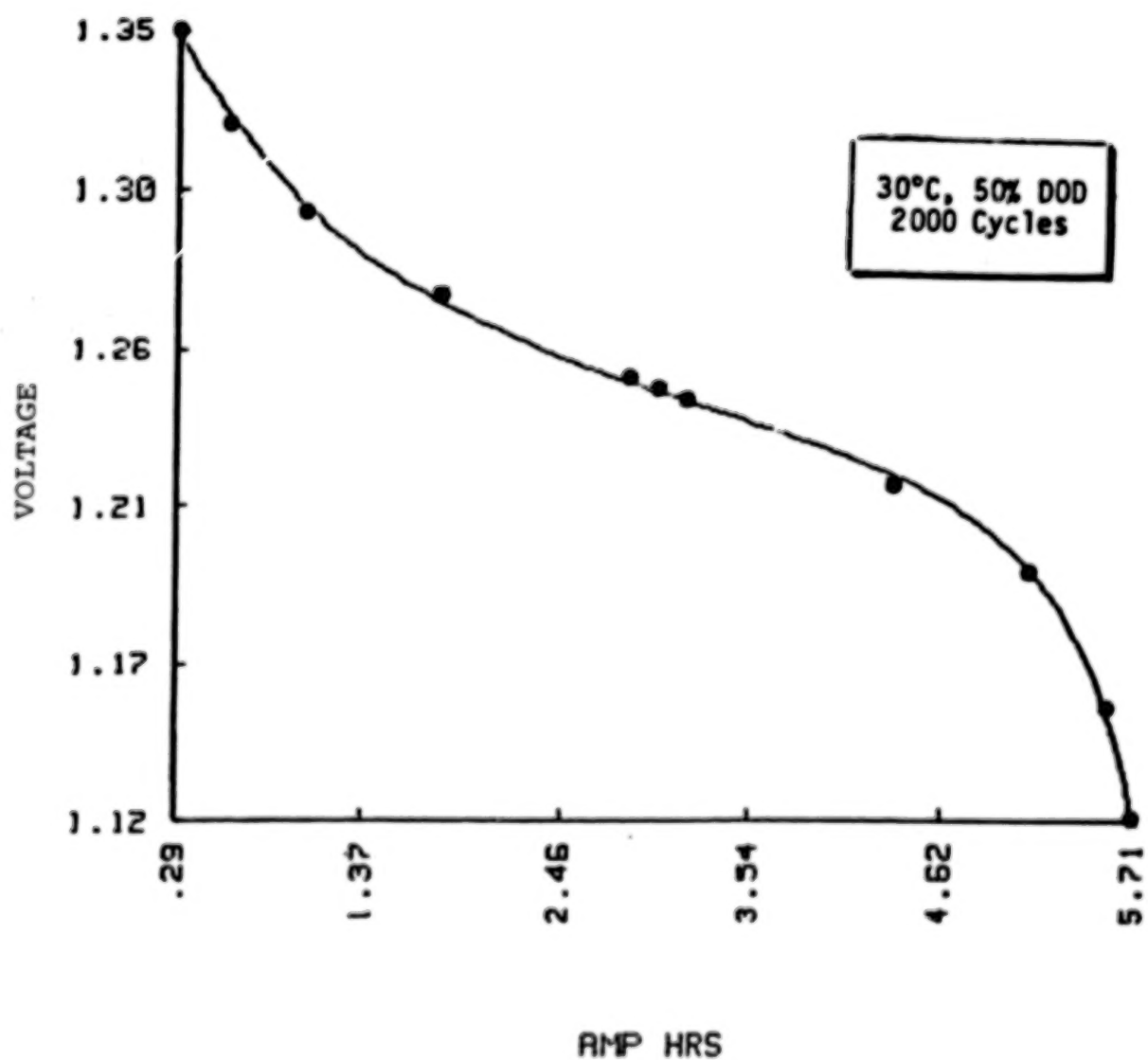


FIGURE 2(b) FIVE PARAMETER DISCHARGE VOLTAGE FIT

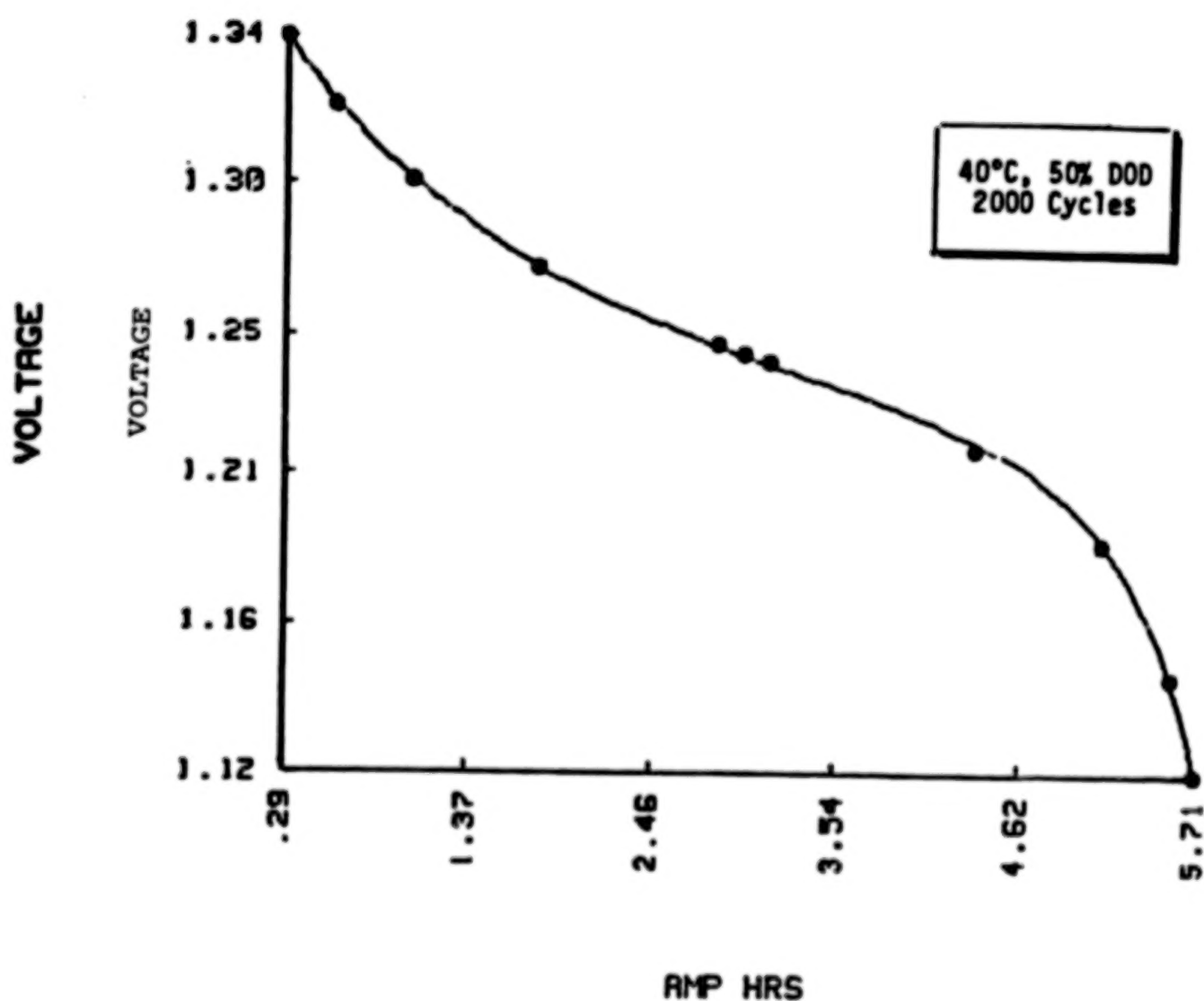


FIGURE 2(c) FIVE PARAMETER DISCHARGE VOLTAGE FIT

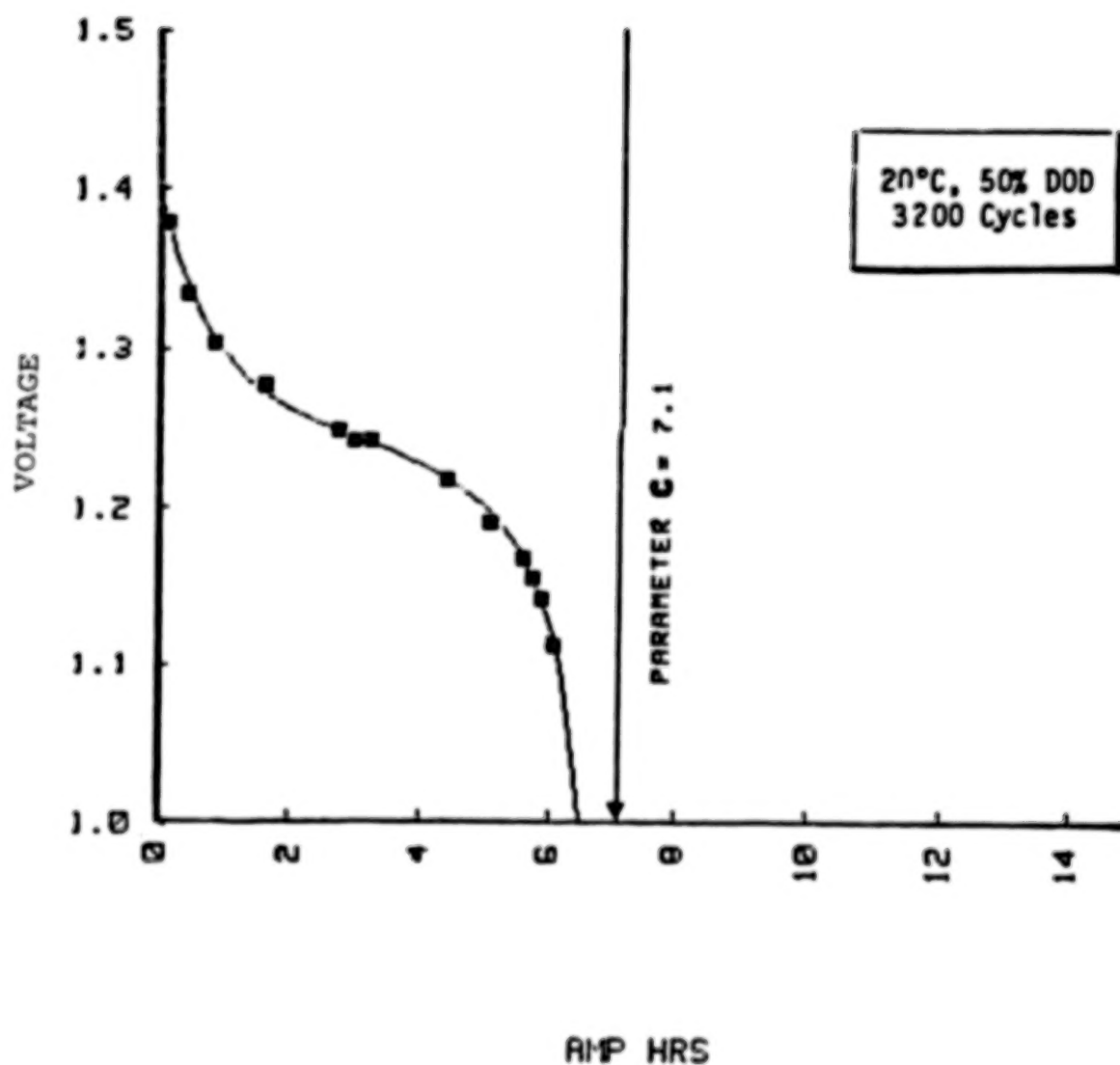
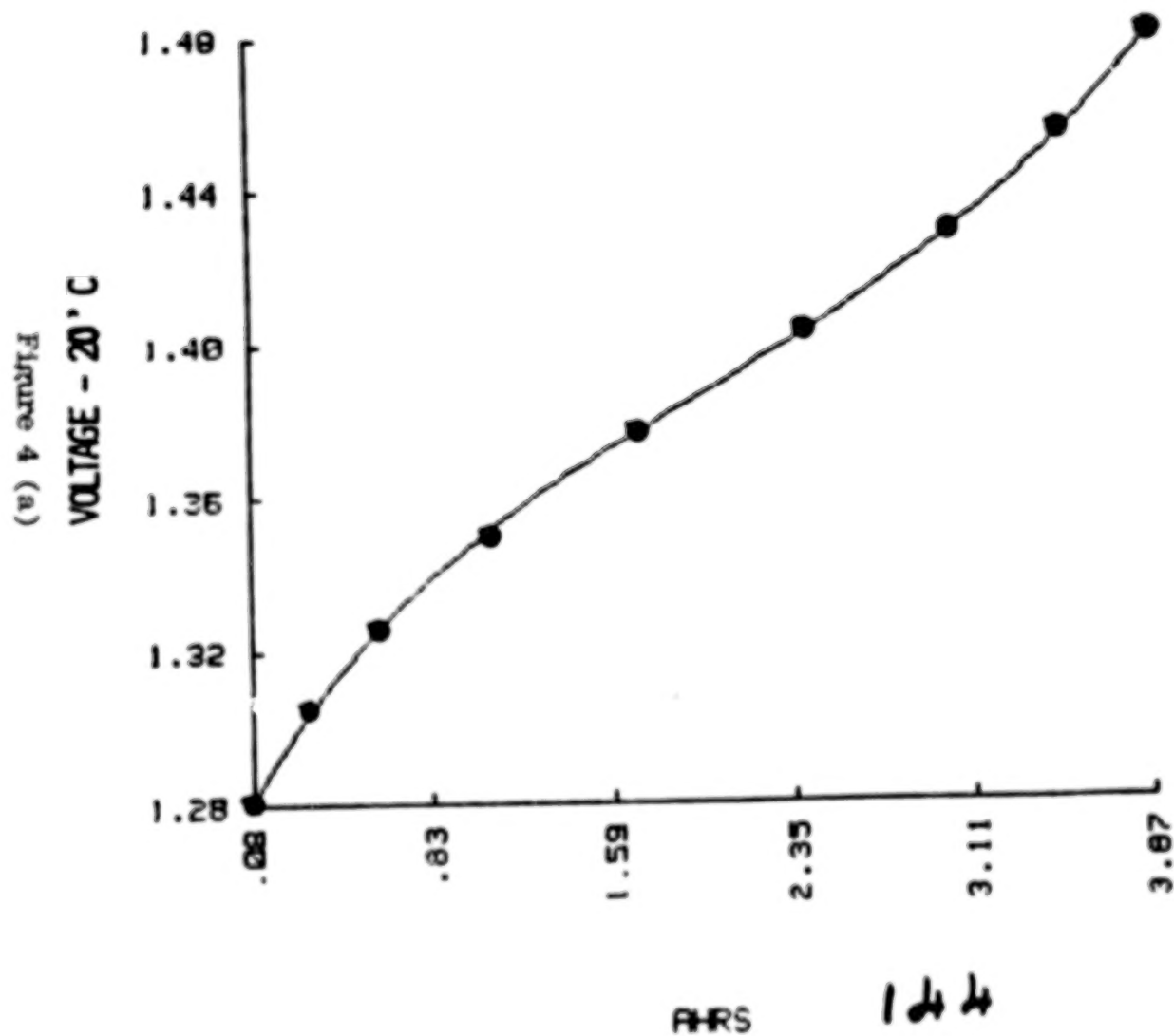


FIGURE 3 FIVE PARAMETER DISCHARGE VOLTAGE FIT

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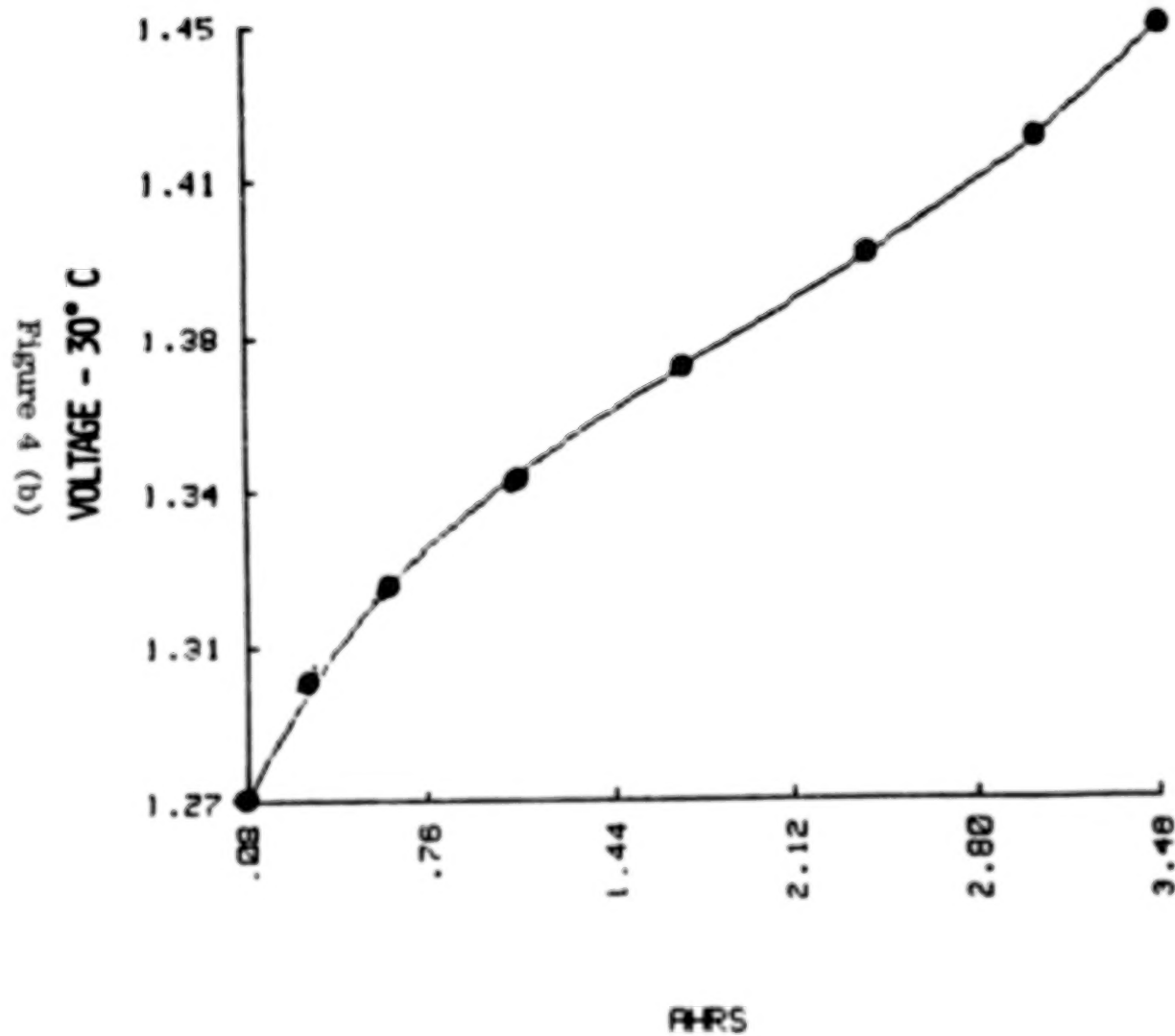
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5-FIT CHARGE 200 CYCLES 35%DOD



124

5-FIT CHARGE 200 CYCLES 35%DOD

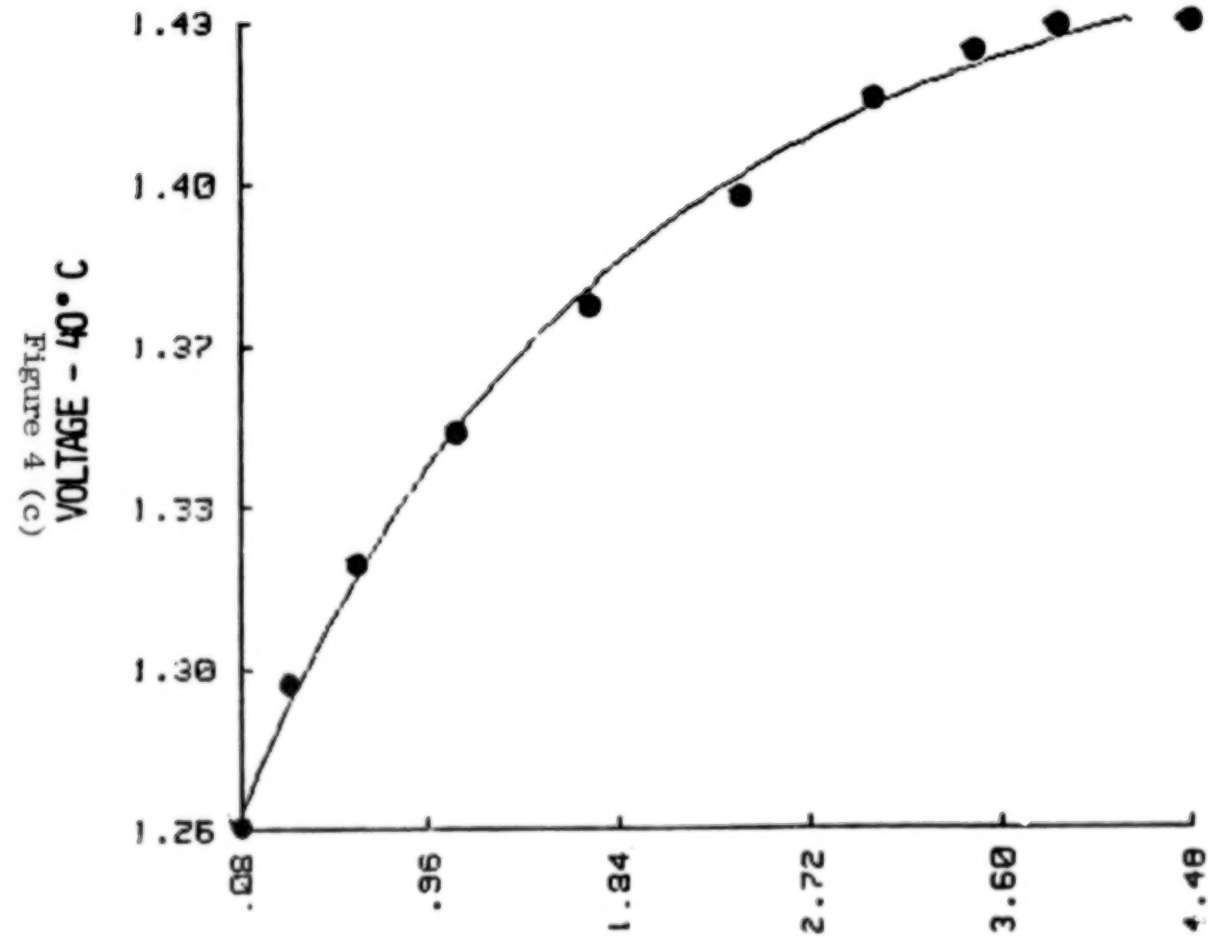


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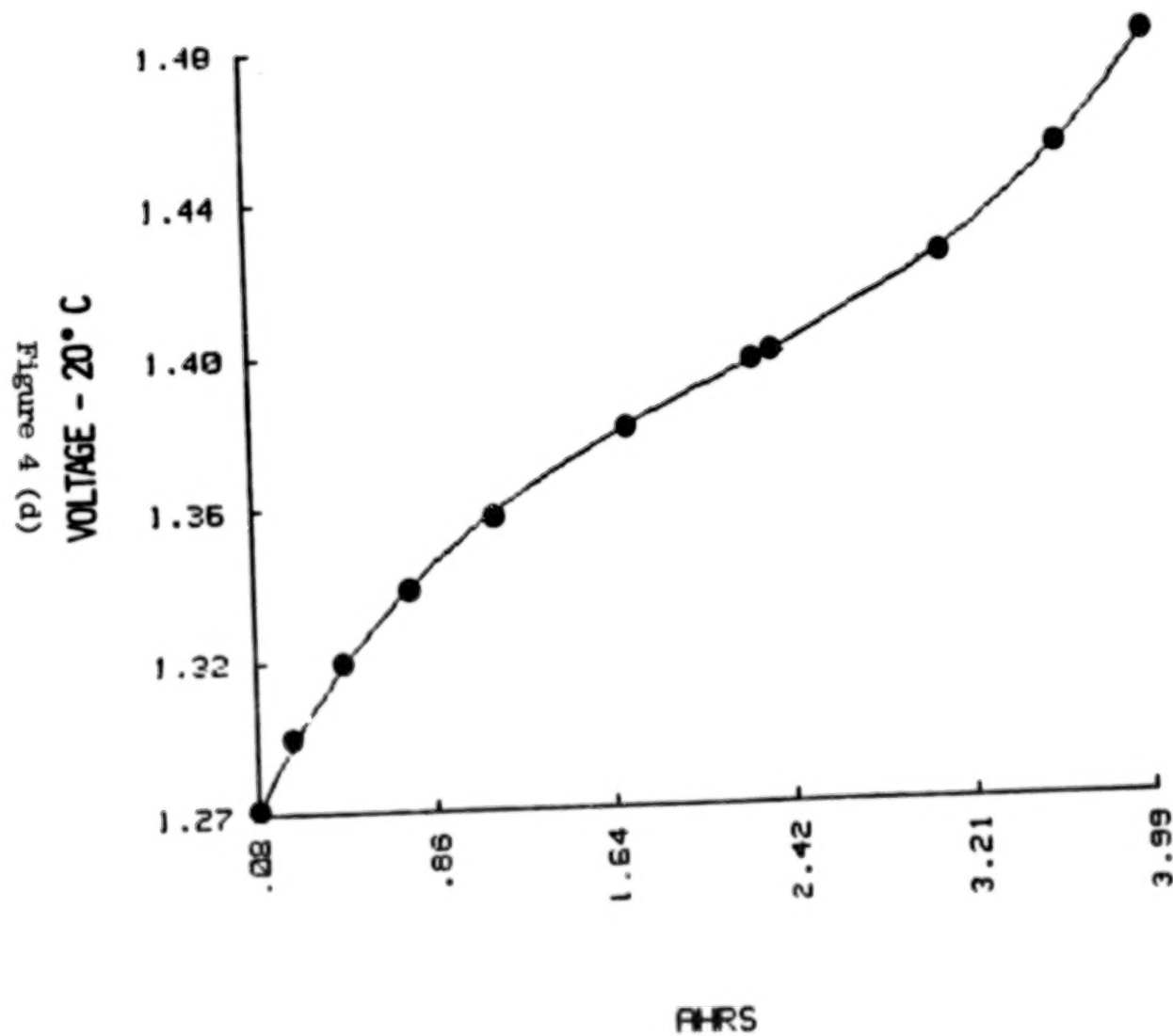
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5-FIT CHARGE 200 CYCLES 35%DOD



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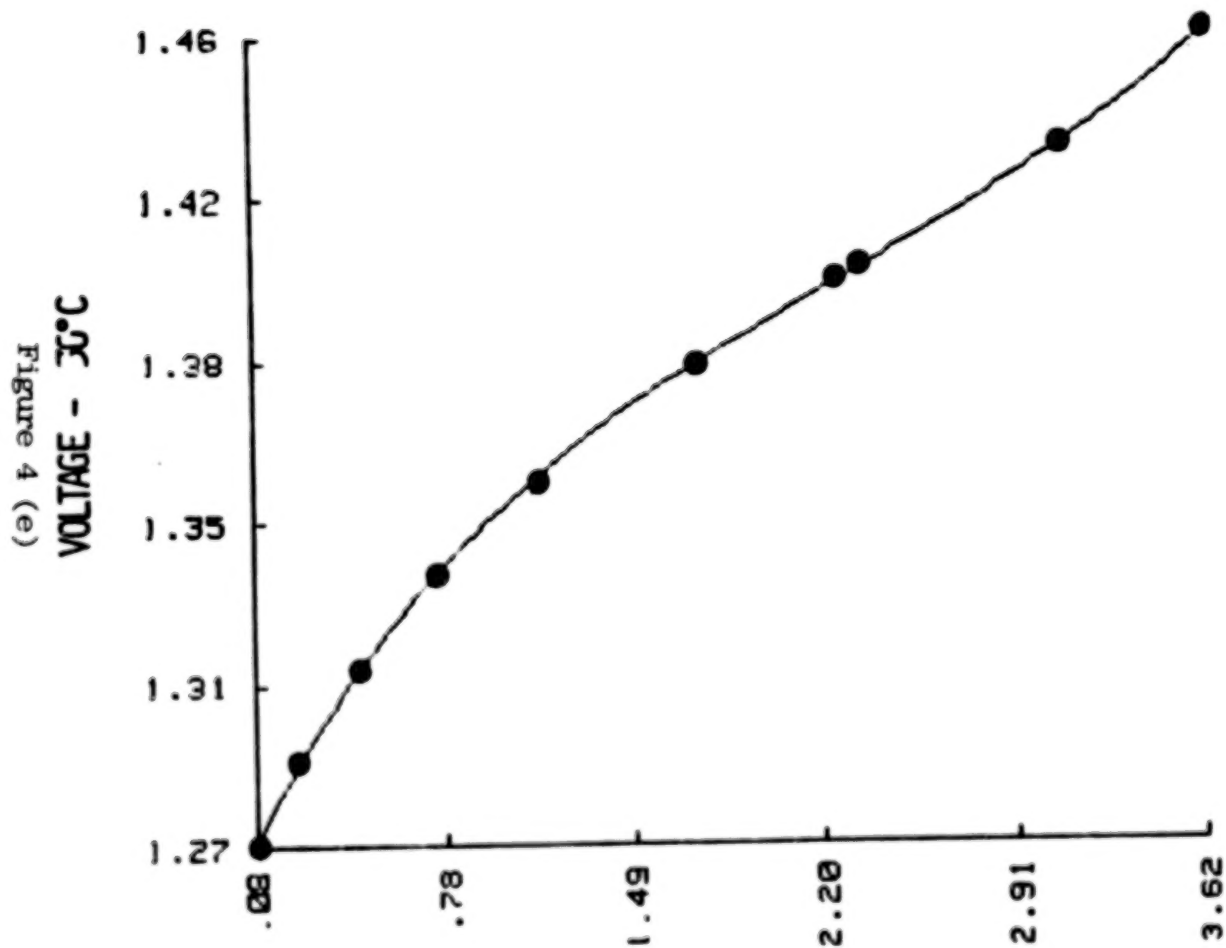
5-FIT CHARGE 3100 CYCLES 35%DOD



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5-FIT CHARGE 3100 CYCLES 35%DOD

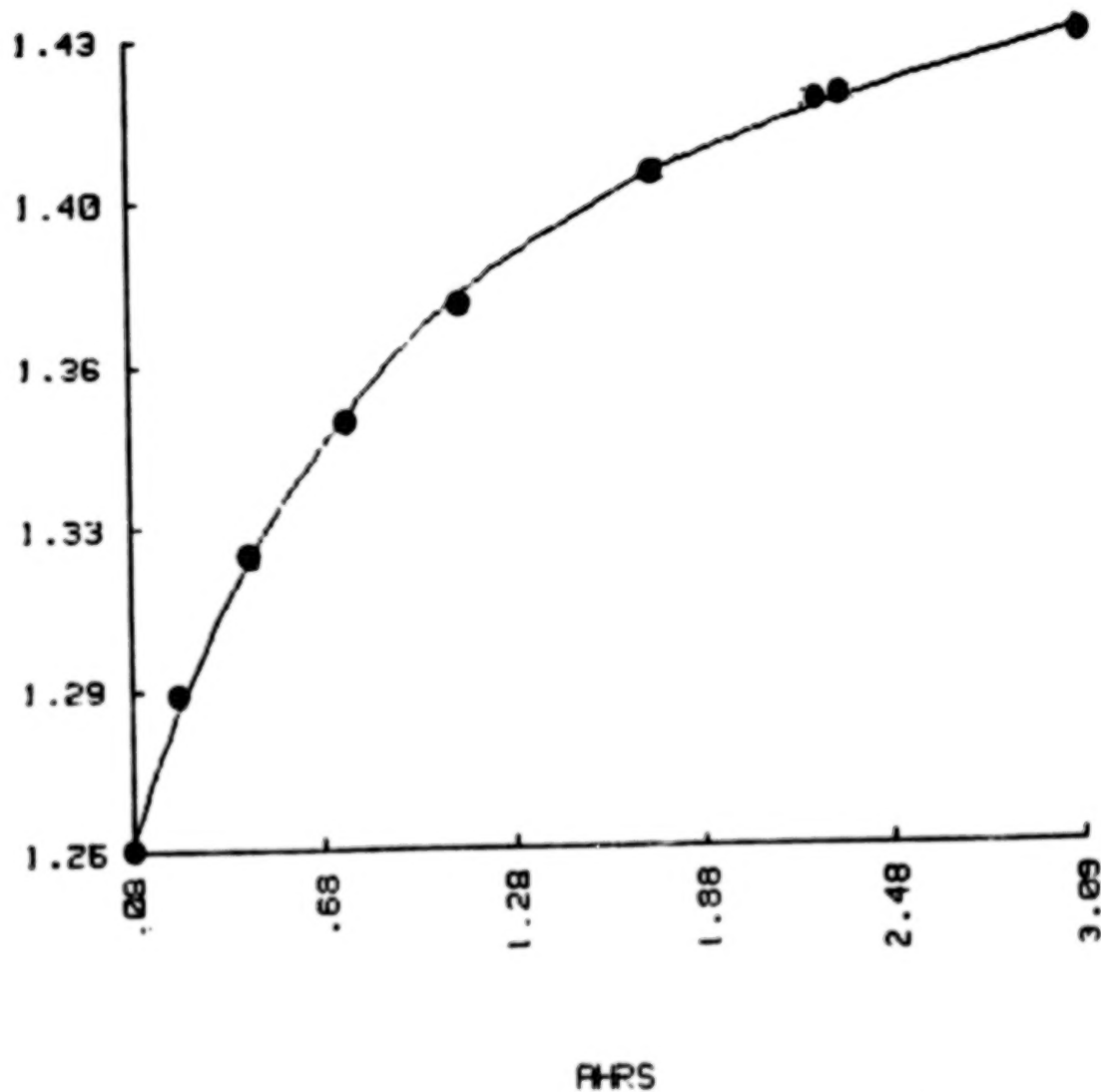


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5-FIT CHARGE 3100 CYCLES 35%DOD

Figure 4 (f)
149



149

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5-FIT DISCHARGE 50%DOD
TEMP 20C

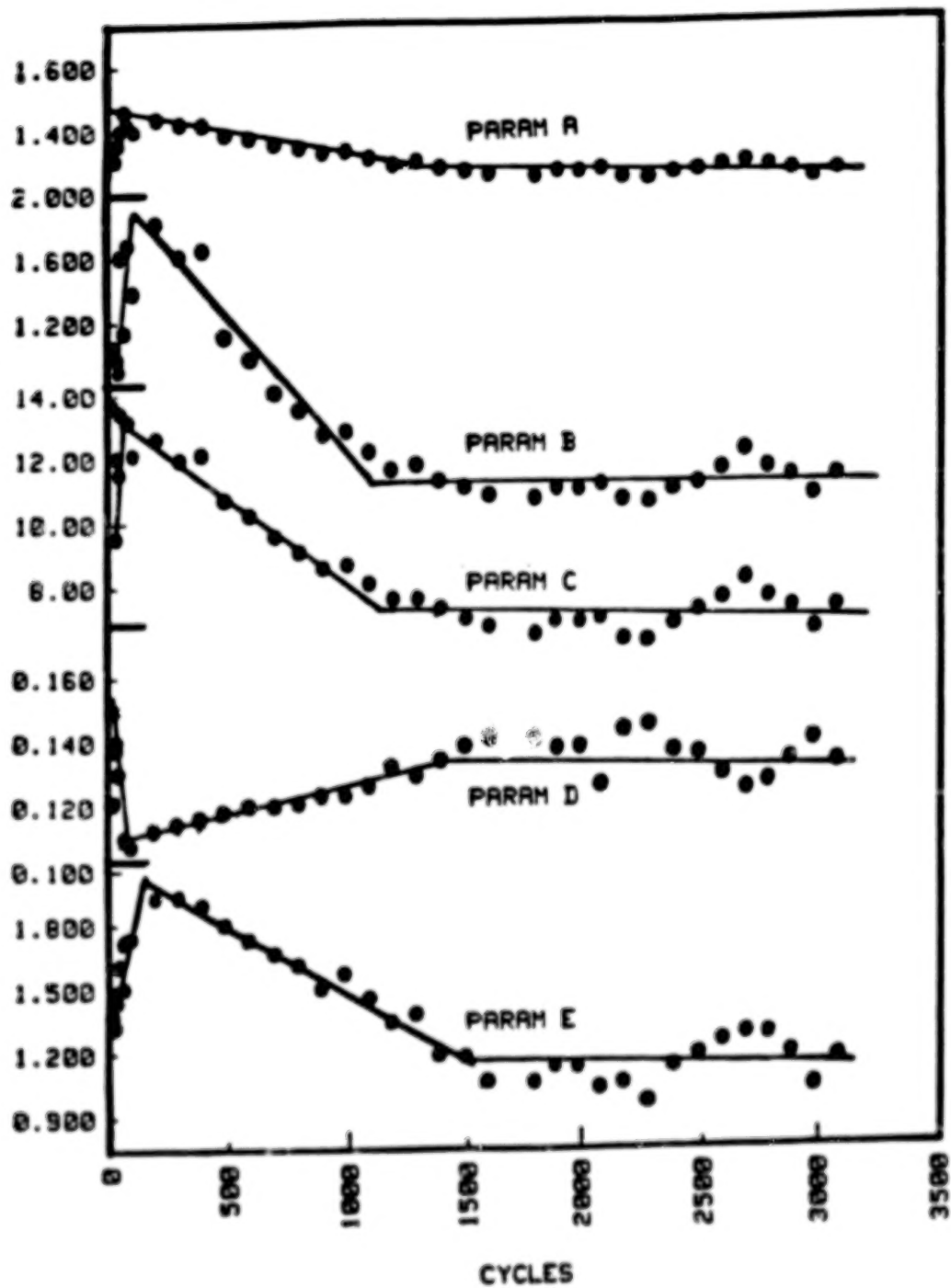


Figure 5

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5-FIT CHARGE 50%DOD
TEMP 20C

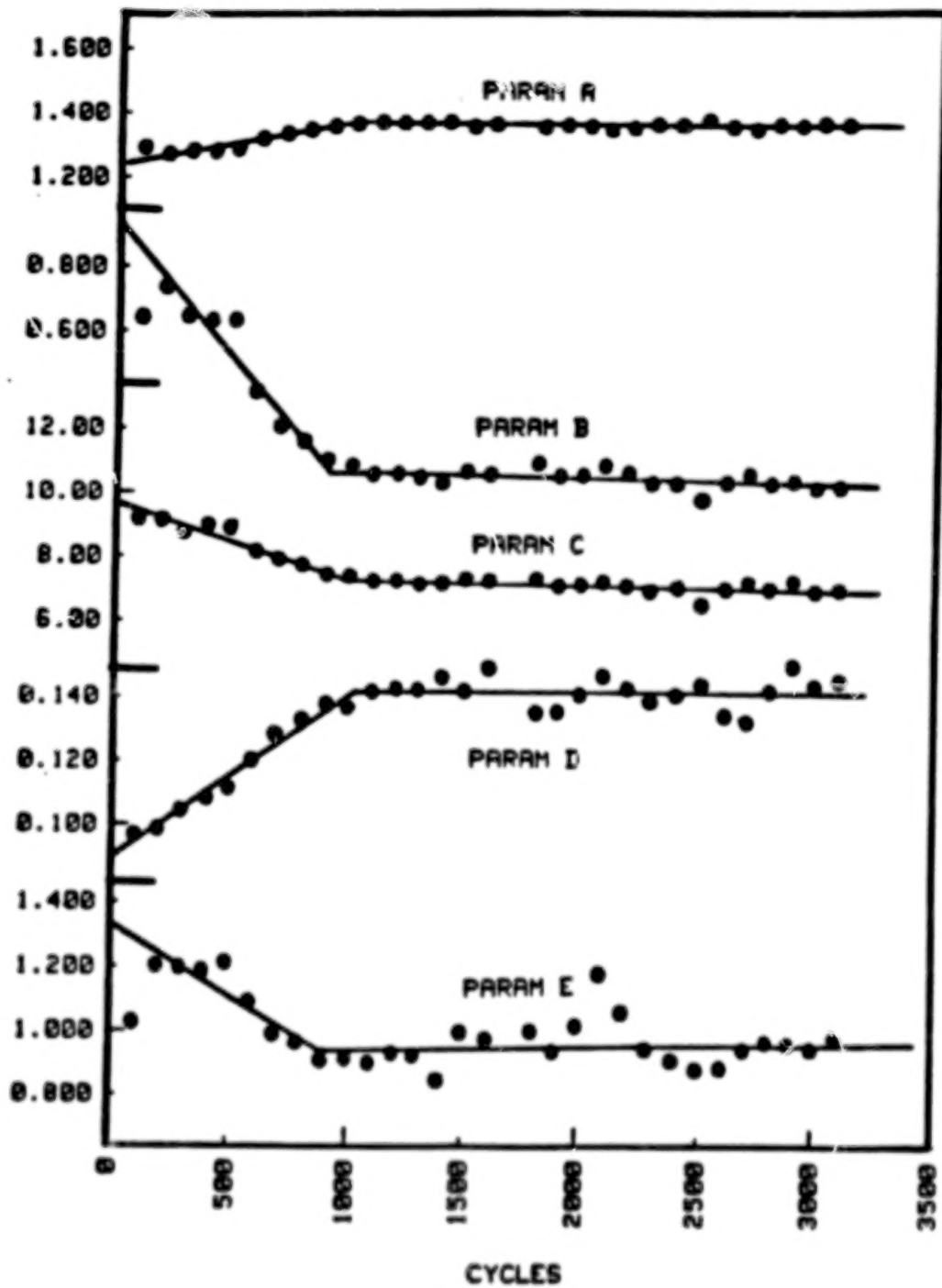


Figure 6

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5-FIT DISCHARGE 50%DOD
PARAM A

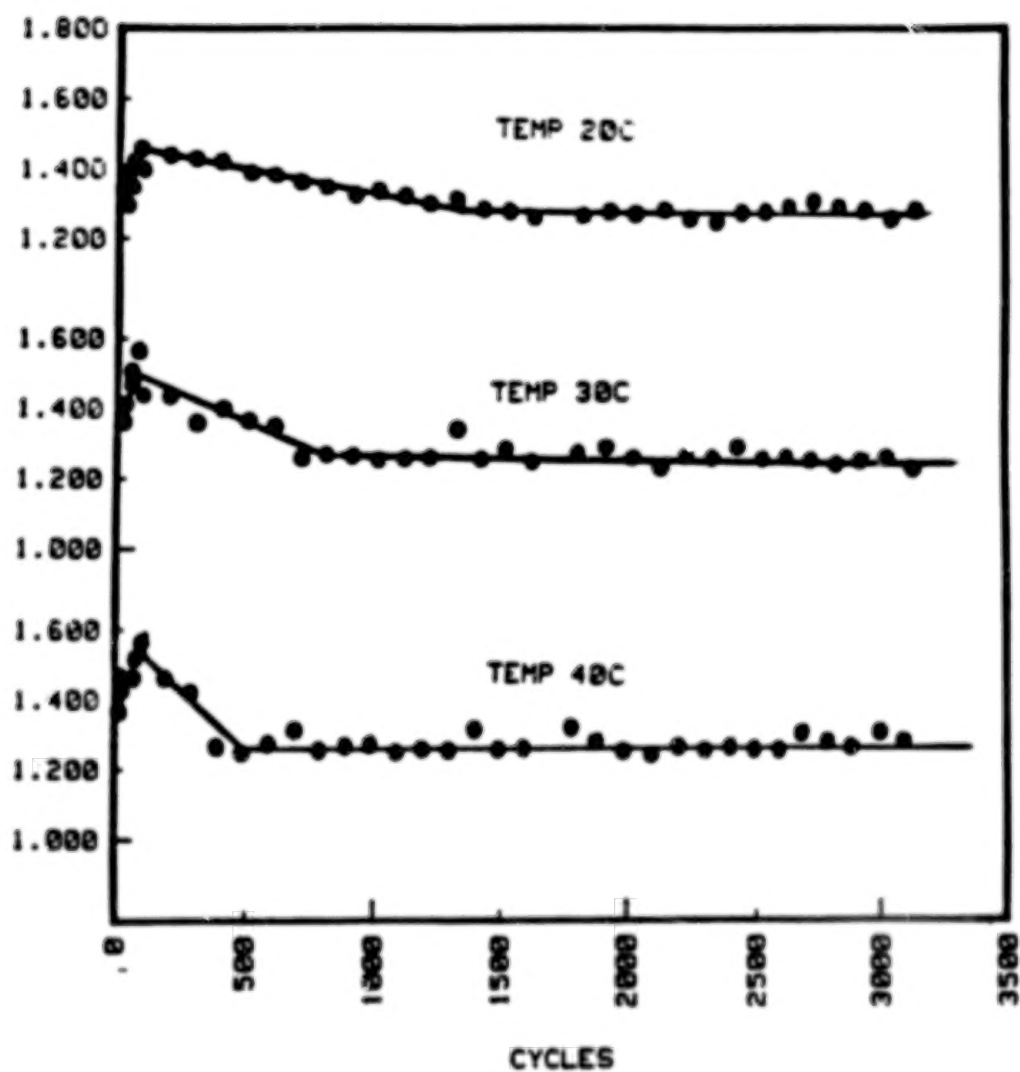


Figure 7 (a)

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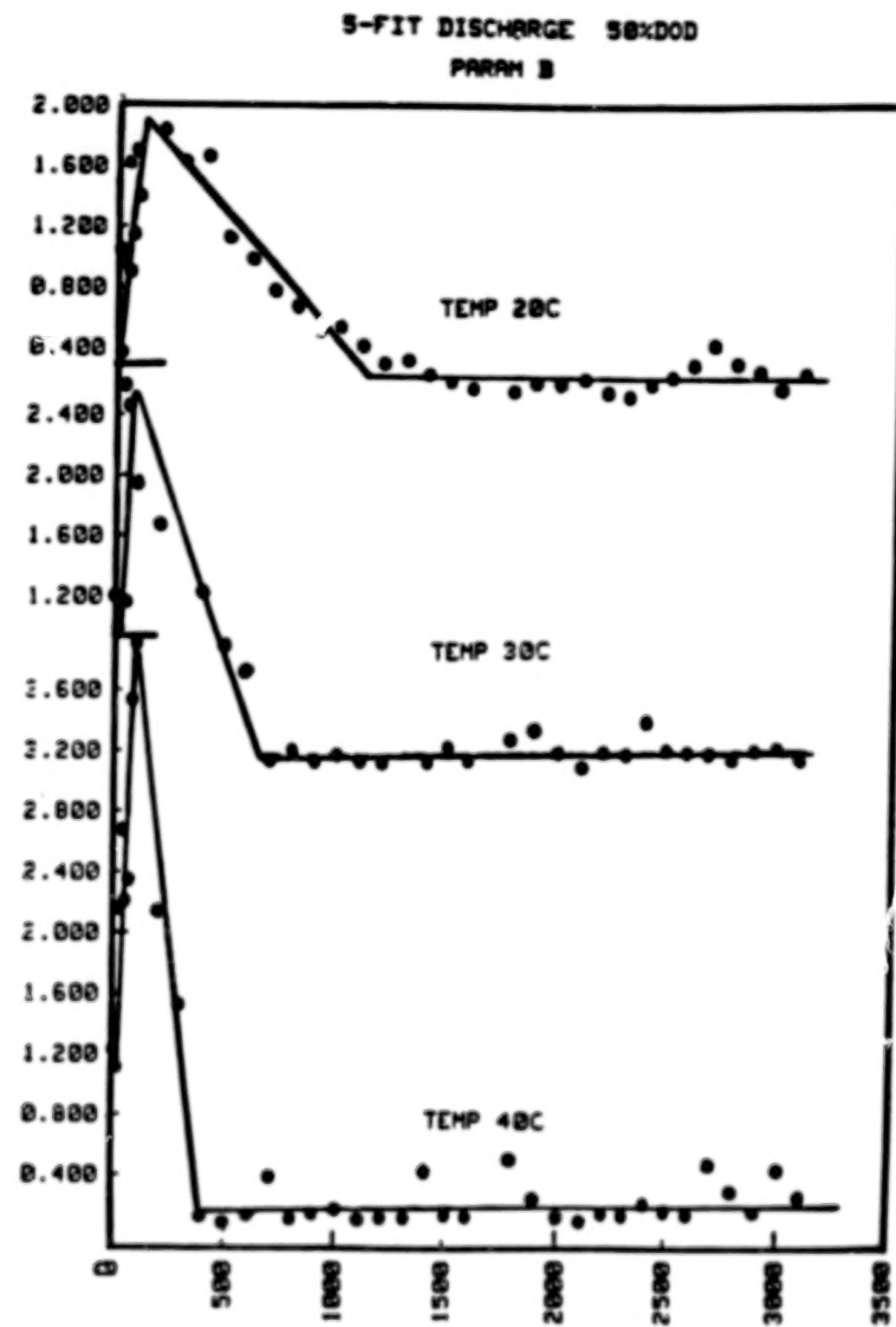


Figure 7 (b)

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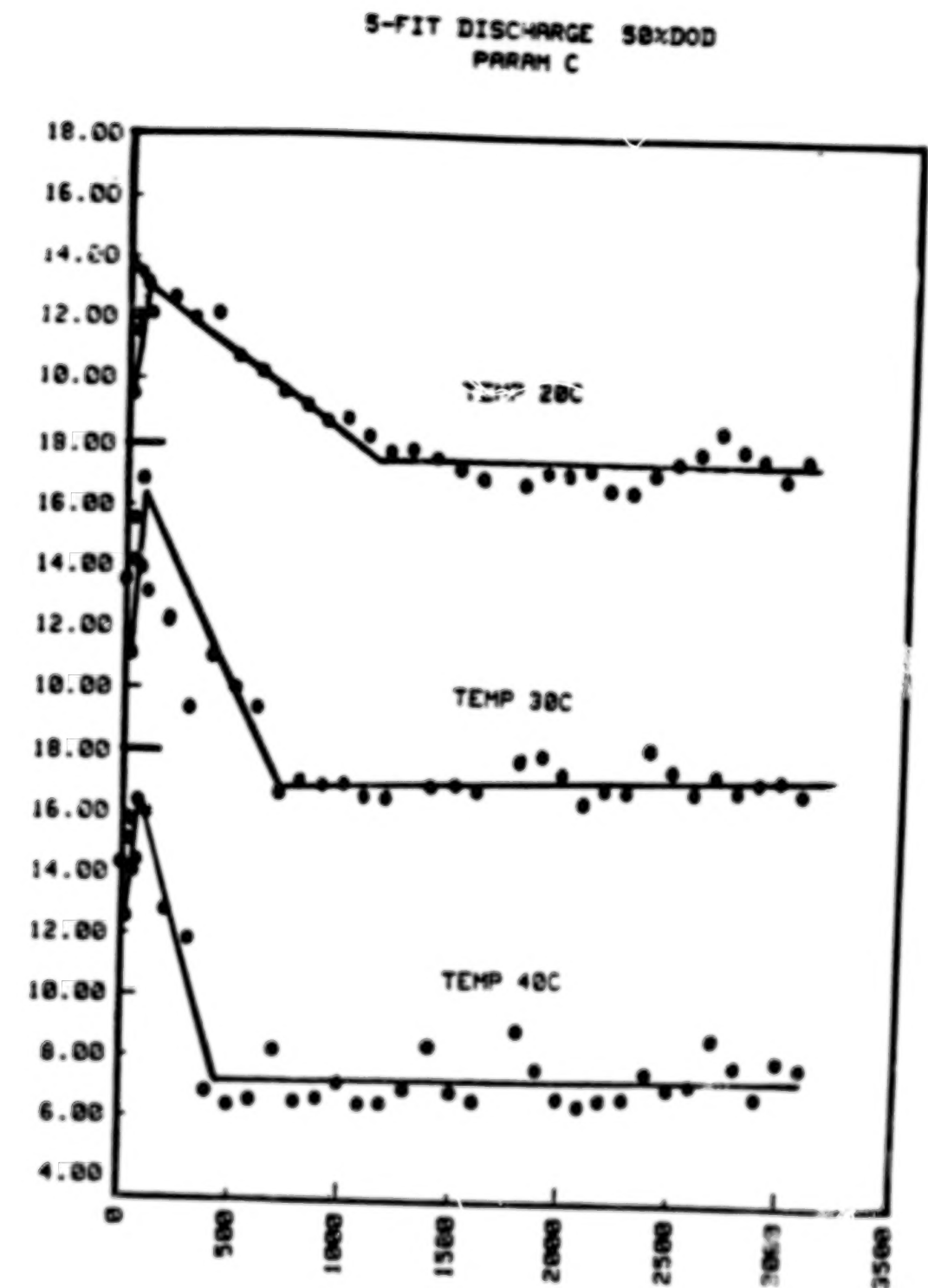


Figure 7 (c)

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5-FIT DISCHARGE 50%DOD
PARAM D

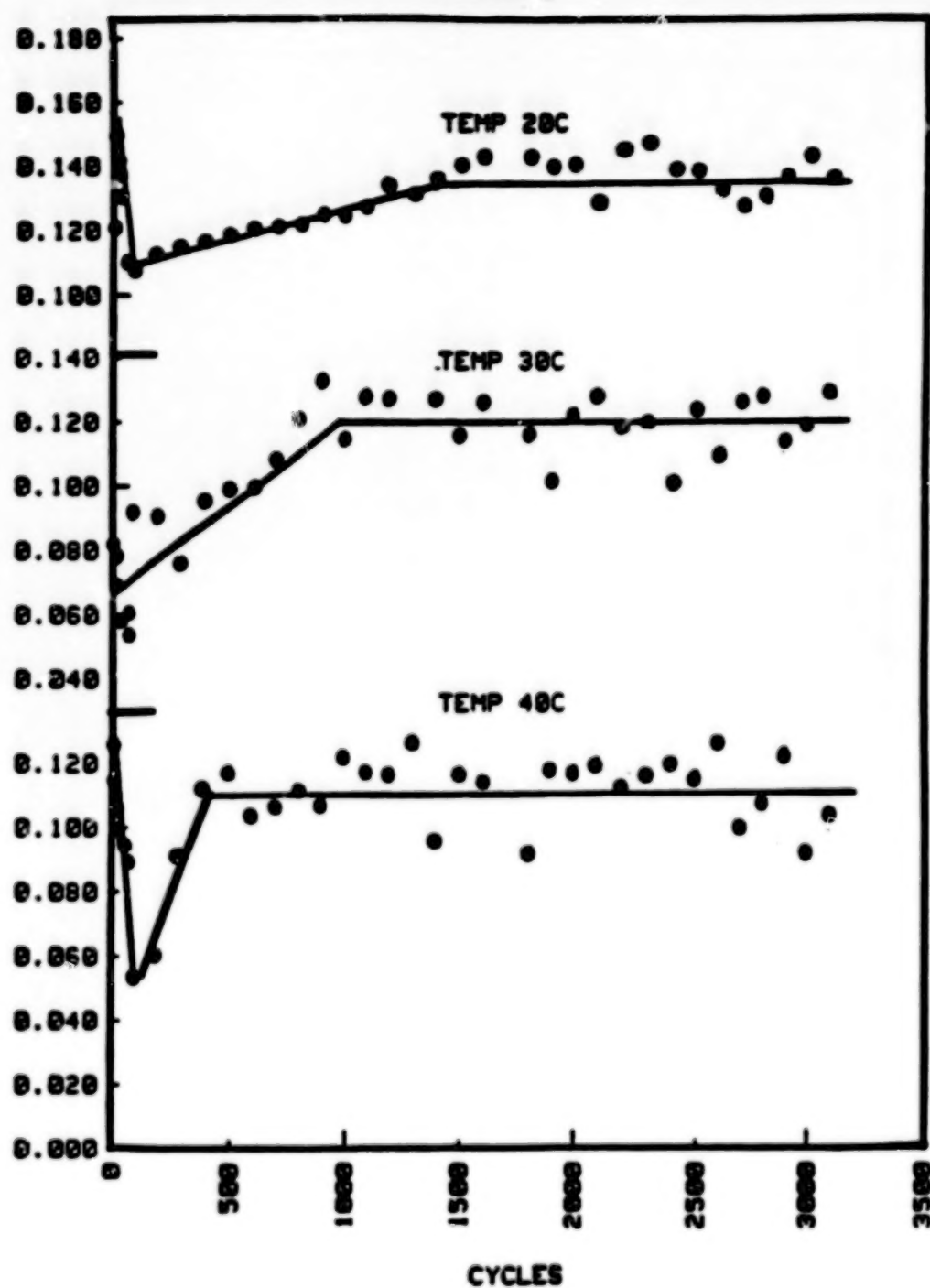


Figure 7 (d)

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5-FIT DISCHARGE 50%DOD
PARAM E

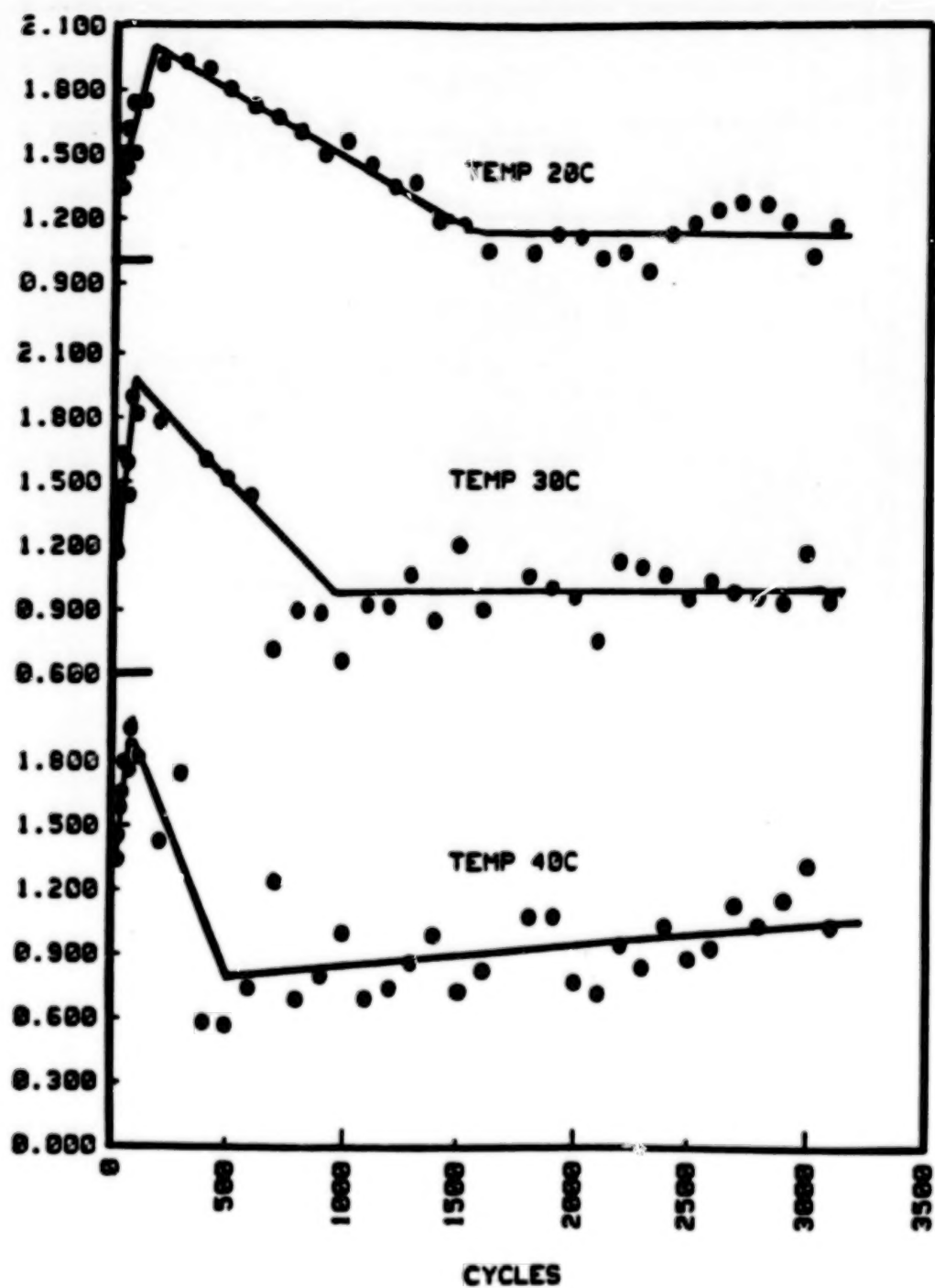


Figure 7 (e)

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5-FIT DISCHARGE 35%DOD
TEMP 28C

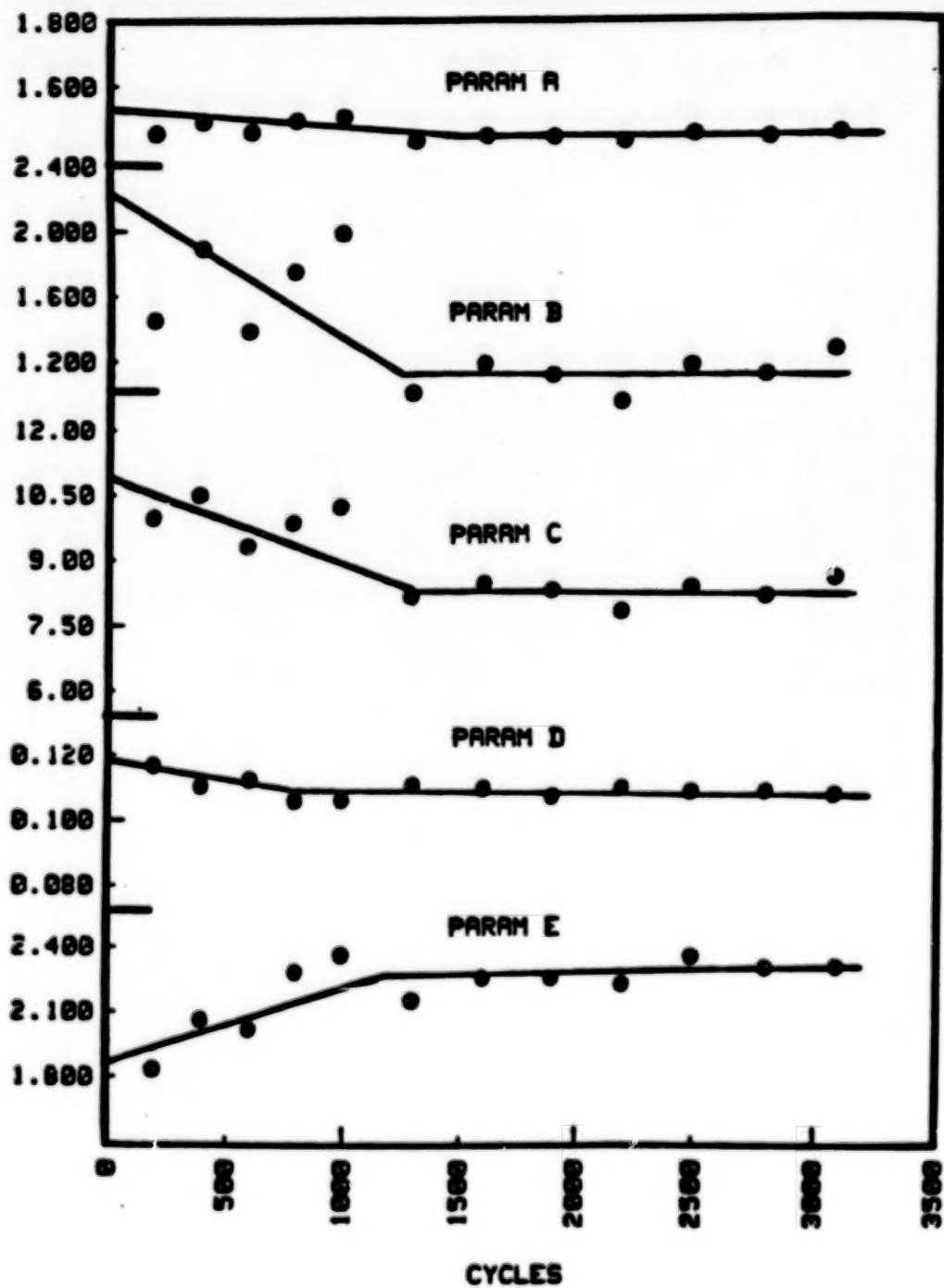


Figure 8

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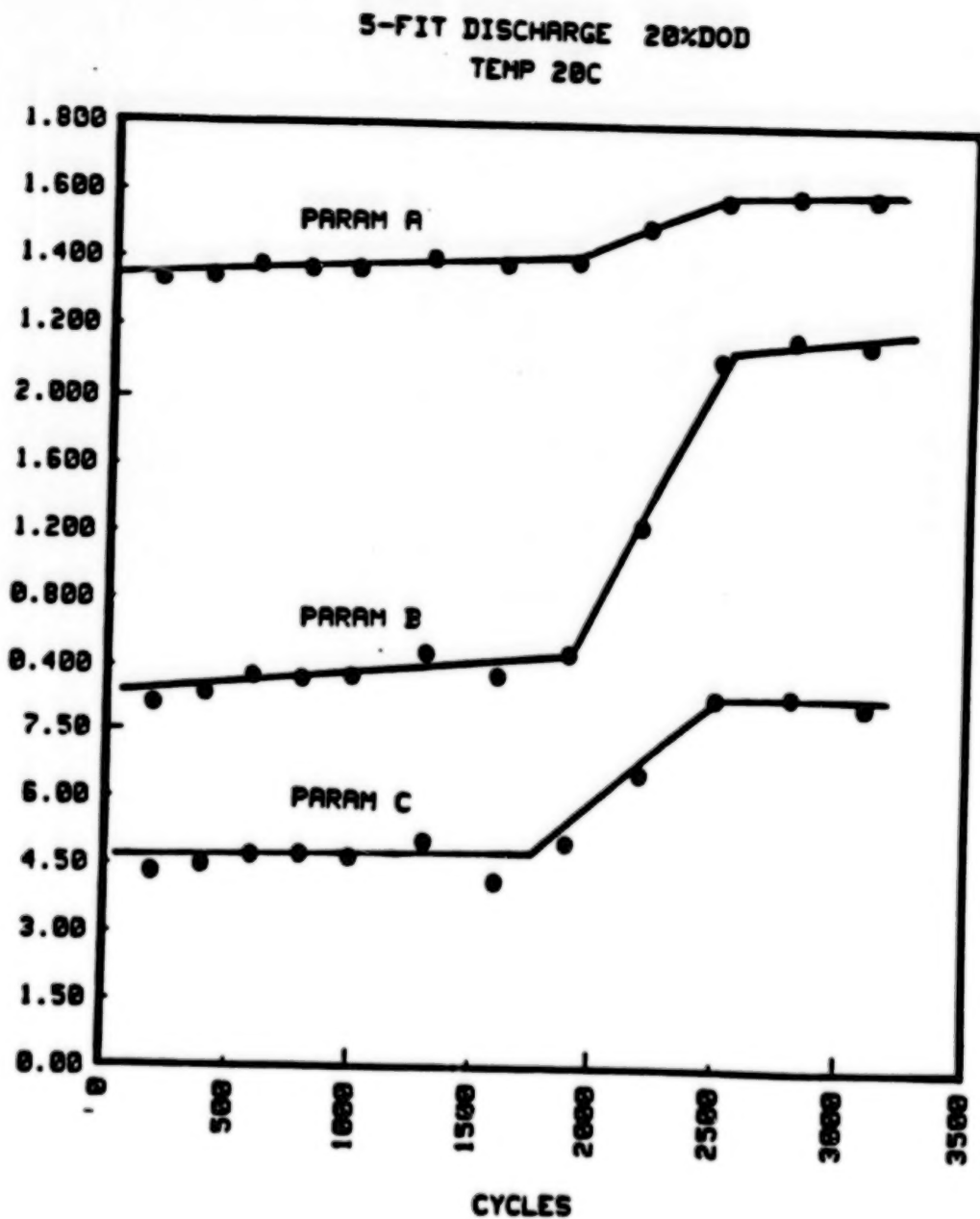


Figure 9

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5-FIT DISCHARGE 20%DOD
TEMP 20C

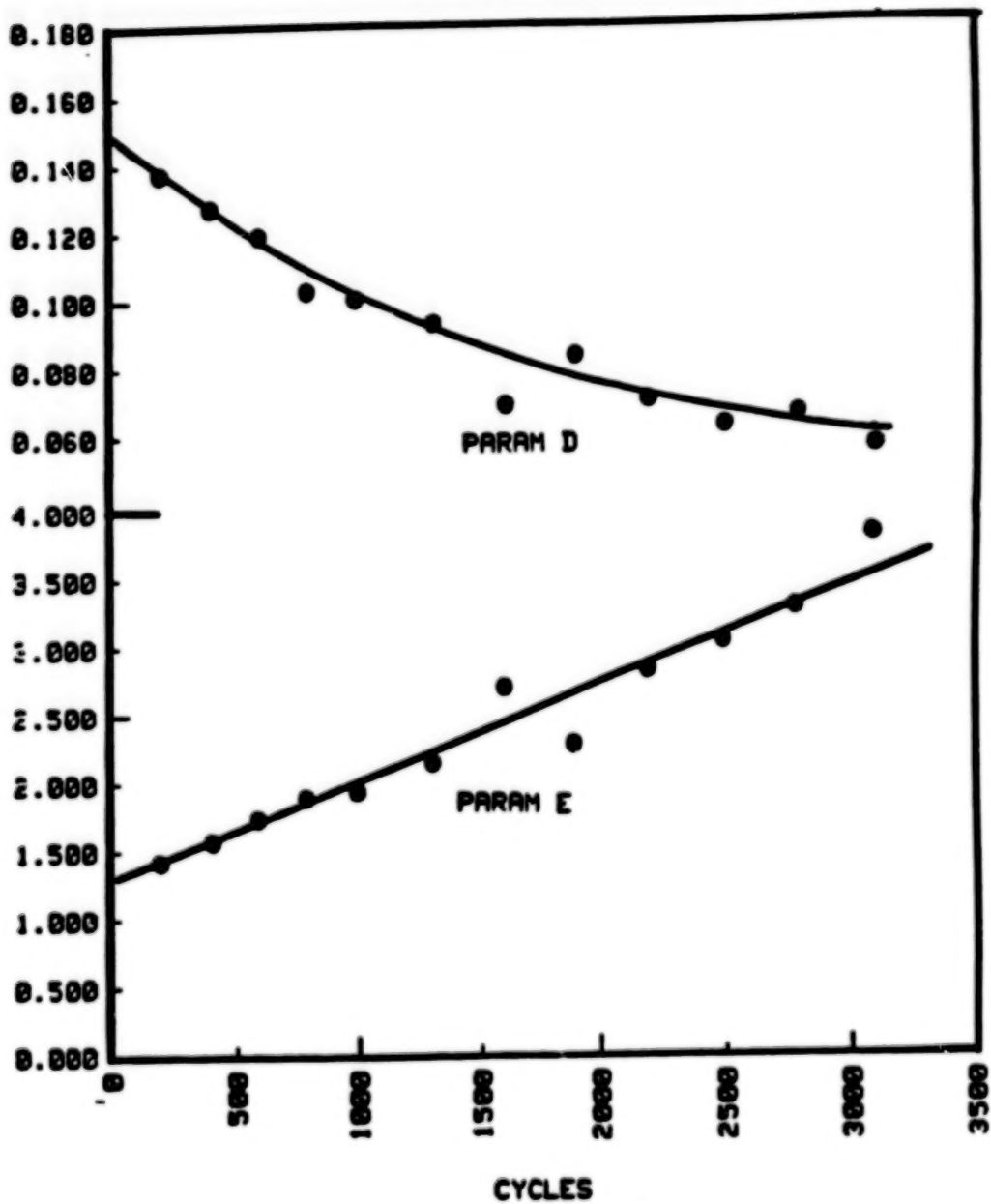
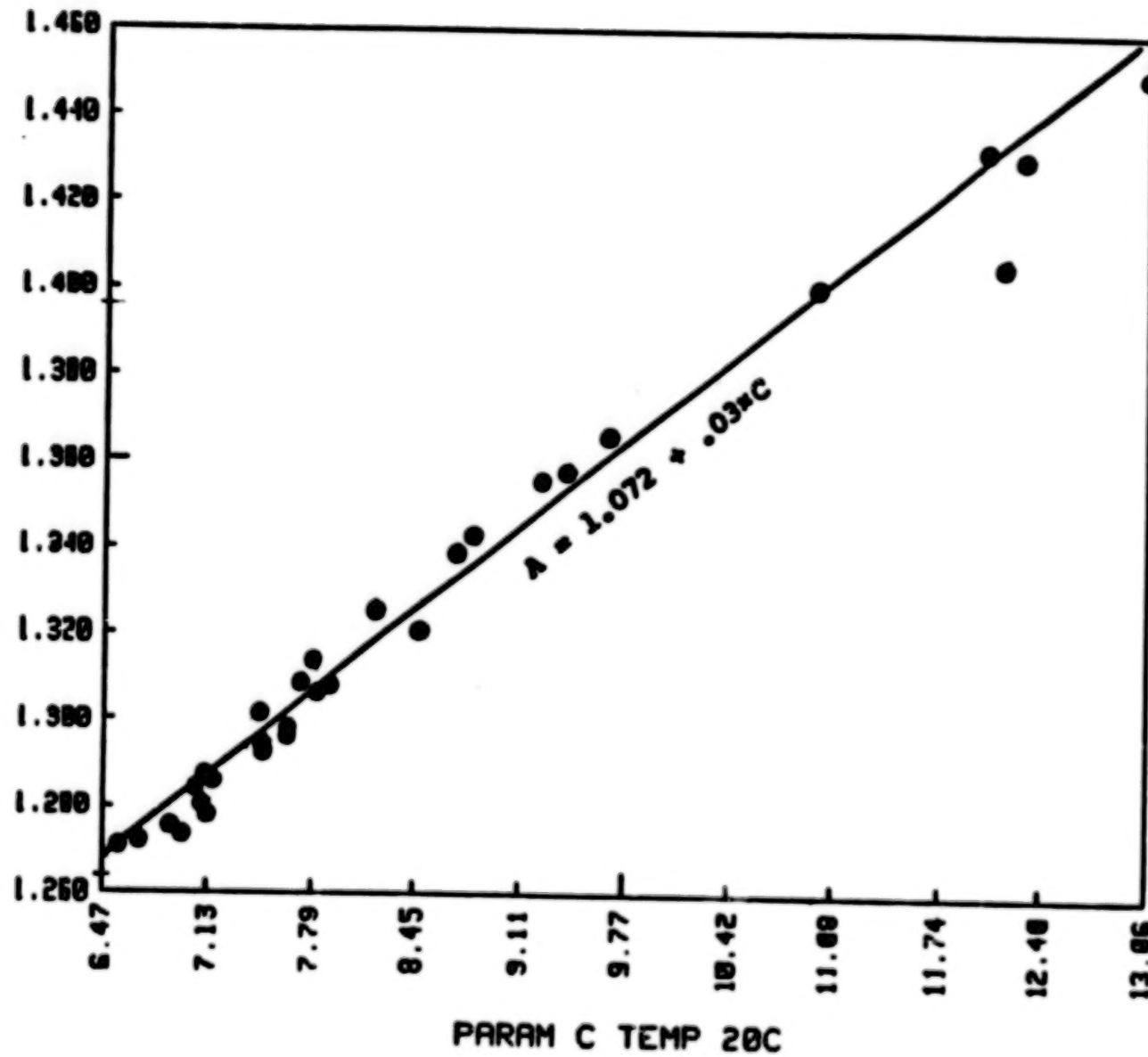


Figure 10

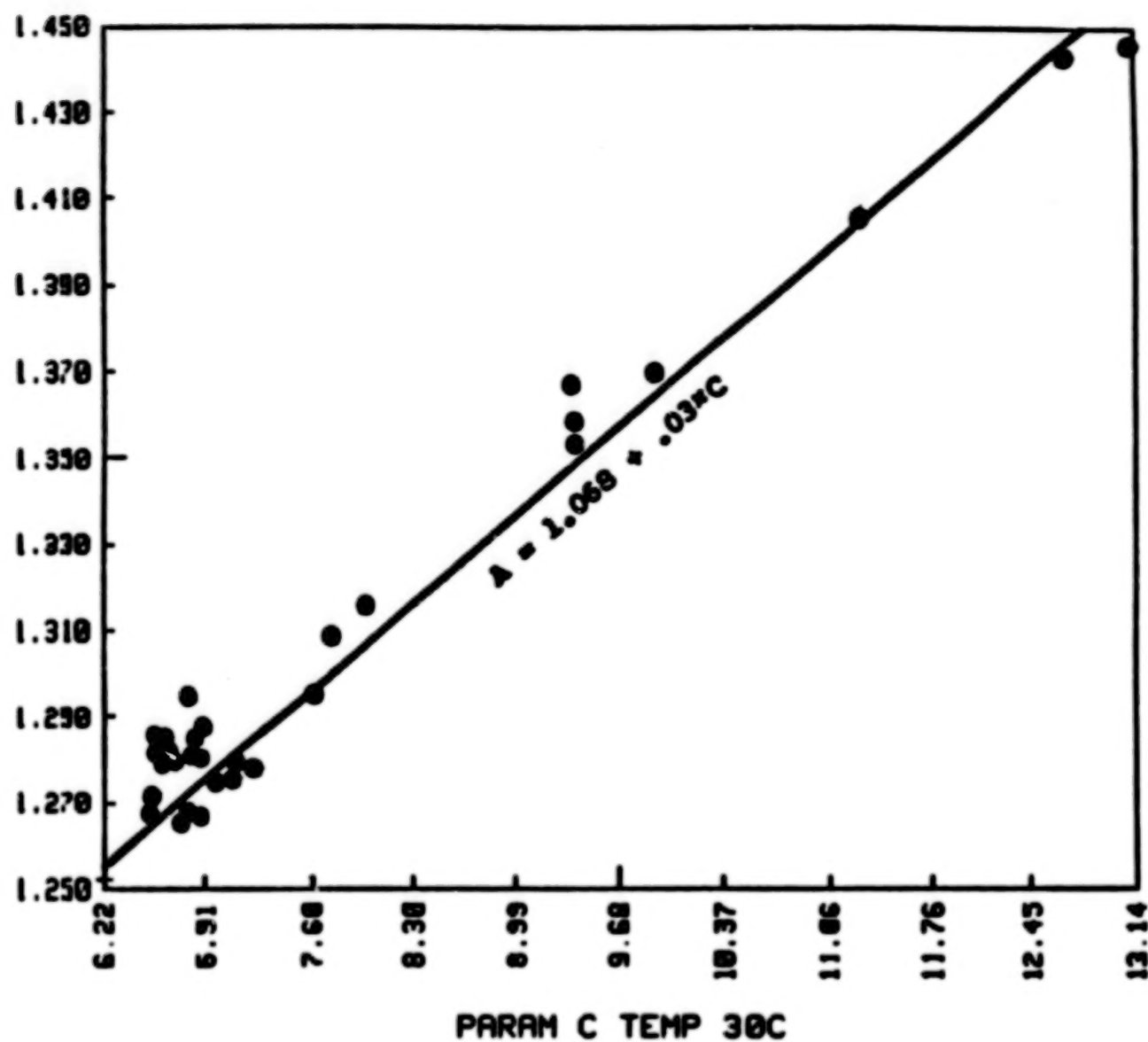
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(a) 11 am 87
PARAM A TEMP 20C



(q) II amgJf
PARAM A TEMP 30C



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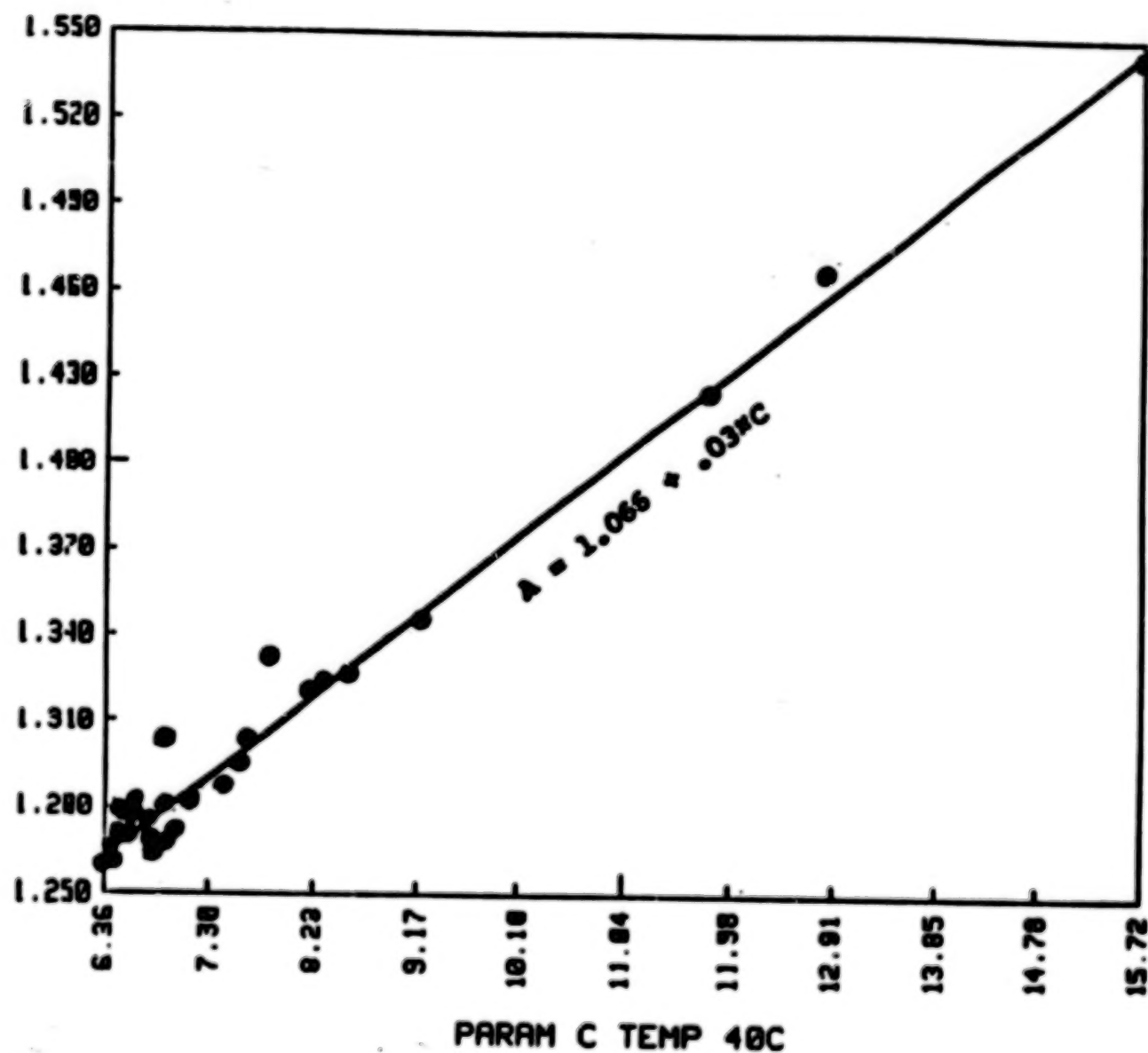


Figure 11 (c)
PARAM A TEMP 40C

PARAM C TEMP 40C

MODELING BATTERY LIFE THROUGH CHANGES IN VOLTAGE FIT COEFFICIENTS

- Introduction
- Five Parameter Fit Equation
- Examples of Charge and Discharge Curve Fits at 20, 30, 40°C and 35% and 50% DoD
- Fit Parameters vs. Cycles for Charge and Discharge
- Effects of Temperature on Fit Parameters
- Effects of Depth of Discharge on Fit Parameters
- Correlations Among Fit Parameters
- Three Parameter Fit
- Conclusions

PITTING VOLTAGE CURVES WITH AN ELECTROCHEMICALLY

DERIVED EQUATION

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ABSTRACT

Previous work is refined and extended to describe the discharge curve of Ni-Cd cells. Several models are discussed which are based on chronopotentiometry theory and on a thermodynamic approach. Emphasis is placed on improvement of the fit for the initial portion of discharge. Equations are presented which improve the fit for all regions of the discharge curve.

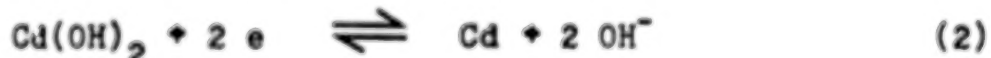
INTRODUCTION

Previous work (ref. 1) applied basic electrochemical principles to the sealed nickel-cadmium cell in an attempt to describe its discharge behavior. An essentially thermodynamic approach was taken to arrive at several related models leading to equations describing the discharge behavior.

The reaction occurring at the positive electrode was taken to be (refs. 2, 3)



and that at the negative electrode (ref. 2)



The Nernst equation describing this cell has the form

$$E = E^{\circ'} + \frac{RT}{F} \ln \frac{a_{\text{NiOOH}}}{a_{\text{Ni(OH)}_2}} - \frac{RT}{2F} \ln \frac{a_{\text{Cd(OH)}_2}}{a_{\text{Cd}}} \quad (3)$$

where $E^{\circ'}$ is the formal potential, R is the gas law constant, F is the faraday, T is the Kelvin temperature and a_i is the activity of species i . Next, the following assumptions were introduced (see ref. 1, p. 2):

- (a) The Cd and Cd(OH)_2 at the negative electrode are present as separate solid phases so that their respective activities are unity.
- (b) The NiOOH and Ni(OH)_2 at the positive electrode are present in a single solid phase, i.e., a solid solution (refs. 4, 5) so that their activities are not unity but, rather, equal to their respective mole fractions:
 $a_i = X_i$.

If no other species are present in the solid solution, then $X_{\text{NiOOH}} + X_{\text{Ni(OH)}_2} = 1$. The discharge equation would then have the form

$$E = E^{\circ'} + \frac{RT}{F} \ln \left[\frac{1-x}{x} \right] - iR_o \quad (4)$$

where x is the state of discharge, i is the discharge current and R_o is the cell resistance. Unfortunately, this simple thermodynamic model did not agree very well with the experimental data (see ref. 1, pp. 1-3, 12-14).

A much more successful equation was arrived at after modification of the simple thermodynamic approach using the method of Barnard, Randell and Tye (ref. 5) in which interactions between species in the solid solution are taken into account. As a result of this modified thermodynamic approach (designated Model II in ref. 1) the Ni-Cd discharge equation became

$$E = E^{\circ'} + \frac{RT}{F} \ln \left[\frac{1-x}{x} \right] + K \frac{RT}{F} (2x-1) - iR_o \quad (5)$$

The term involving K represents a correction due to species interaction. A value of K=0 represents ideal behavior and corresponds to the simple thermodynamic approach. Values of K=+1 or -1 represent respectively positive and negative deviation from ideality. The case where K=2 corresponds to the borderline between a single-phase and a two-phase system. K was treated as an adjustable parameter; after a least squares fit the Model II discharge equation was found to be

$$E = 1.294 + \frac{RT}{F} \ln \left[\frac{1-x}{x} \right] + 0.789 \frac{RT}{F} (2x-1) - iR_o \quad (6)$$

Typical results are shown in Figure 1, curves A and B. Calculated curves fit experimental data quite well for the latter 50% or so of the discharge. Unfortunately, the fit was not nearly as good for the initial portion of the curve, which is of much greater interest and importance. In addition, the fit was poorest for the first 25% of discharge which is probably of greatest importance.

Another promising model (designated Model IV) was based on the theory of chronopotentiometry, which is a constant current technique. For a description of this technique consult reference 6 and reference 1, pp. 8-9. The discharge curves are treated as chronopotentiograms which leads to a discharge equation of the form

$$E = 1.294 + \frac{RT}{F} \ln \left[\frac{1-x^{1/2}}{x^{1/2}} \right] - iR_o \quad (7)$$

Typical results are shown in Figure 1, curves C and D. Unfortunately, this equation also did not fit well in the initial portions. In fact the fit was, overall, not as good as the modified thermodynamic model.

RESULTS OF THE PRESENT STUDY

In this paper, refinement and extension of the previous work is described with special emphasis placed on improvement of fit for the initial portion of the discharge.

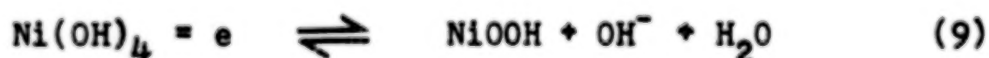
CHRONOPOTENTIOMETRIC MODELS

the chronopotentiometric approach (Model IV) was pursued first. In spite of the fact that this approach previously led to a somewhat poorer fit than the modified thermodynamic approach (Model II), it was felt that the former might be more easily modified to achieve a better fit. At first, it appeared that a slight mathematical shift of the calculated curve might bring it more in line with experiment. An equation was tried of the form

$$E = 1.294 + \frac{RT}{F} \ln \left[\frac{1 - (x+f)^{1/2}}{(x+f)^{1/2}} \right] - iR_o \quad (8)$$

Unfortunately, the "best fit" value of f proved to be zero, meaning that a simple shift was not sufficient.

Upon close examination of the initial portion of the experimental discharge curve, it is evident that there is distortion from the shape of a normal chronopotentiogram (see ref. 6). In fact, such a shape could result from the merging of two chronopotentiograms, i.e., a two-step process. To develop this idea further, let us suppose that on "preconditioning" and fully charging, a certain portion of the nickel in the active layer is in the Ni(IV) state. On subsequent discharge, reduction of Ni(IV) to Ni(III) would precede reduction of Ni(III) to Ni(II). The reduction of Ni(IV) to Ni(III) can be written as



The cell potential for this first step can be expressed as

$$E = 1.47 + \frac{RT}{F} \ln \left[\frac{1-(x+1-f)^{1/2}}{(x+f)^{1/2}} \right] - iR_o; x < f \quad (11)$$

where f is the fraction of active nickel present as Ni(IV). The corresponding equation for the second step is

$$E = 1.294 + \frac{RT}{F} \ln \left[\frac{1-(x-f)^{1/2}}{(x-f)^{1/2}} \right] - iR_o; x \geq f \quad (12)$$

To be consistent with the previous work, this approach is designated "Model IV A". Least squares treatment of several experimental discharge curves yielded a best fit value of $f=7.26\%$ (or 0.0726). Typical results are shown in Figure 2, curves A and B. This approach provided no improvement over the simple chronopotentiometric approach of Model IV.

In a variation of the above approach, equation (12) was replaced with equation (7). This approach is designated "Model IV B". Least squares analysis of experimental discharge curves yielded a best fit value of $f=3.10\%$ (0.0310); typical results are shown in Figure 2, curves C and D. Results are comparable to Model IV with no improvement. In a final variation, designated "Model IV C", equation (11) was coupled with equation (8). Least squares analysis yielded a best fit value of $f=5.94\%$ (0.0594); typical results are shown in Figure 2, curves E and F.

The equations used for the chronopotentiometry-based models are summarized in Table 1; a comparison of errors is shown in Table 2. Model IV C does provide some improvement over Model IV for the initial portions of the discharge curve. However, the fit of experimental data is still better with the thermodynamic approach. In addition, there has been no experimental evidence for the presence of Ni(IV) in the active phase.

THERMODYNAMIC MODELS

Since the thermodynamic approach still seemed to provide a better fit, even in the initial portions of the discharge, this method was pursued further. Upon examination of the Model II discharge curves (see Figure 3 A,B) there appears to be three different regions: In the range 0-15% discharge the data points lie above the calculated curve. From 15-40% discharge the points lie below the curve. Beyond 40% discharge the curve follows the data quite well. This behavior can be rationalized perhaps by noting that although the active phase at the positive electrode is a single phase, it need not be uniform. Initially it contains virtually entirely Ni(III). As the discharge proceeds, Ni(II) builds up. It seems reasonable, then, that the deviation from ideality might not remain the same throughout the discharge. With this in mind, a least squares analysis of equation (5) was carried out to determine the best values of K for each of the regions 0-15%, 15-40% and 40-100% discharge. Using a number of individual discharge curves, best fit values were found to be 0.014 for 0-15% discharge, 1.374 for 15-40% discharge and 0.918 for 40-100% discharge. For consistency with previous work, this approach is designated "Model II A". Typical results are shown in Figure 3, curves C and D. There is significant improvement in all regions of the discharge curve.

In an attempt to improve the fit still further, the ranges were changed slightly and the process repeated (Model II B). For the range 0-10% discharge, K was determined to be -0.326; for the range 10-40% K was 1.116 and for 40-100% K was 0.918. Typical results are shown in Figure 3, curves E and F.

The equations used for the thermodynamic-based models are summarized in Table 3; a comparison of errors is shown in Table

4. Both models II A and II B show improvement in all regions of the discharge. Model II B, however, appears to provide a somewhat better fit than does Model II A.

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4. Barnard, R., Randell, C. F. and Tye, F.: J. Appl. Electrochem. 10, 109 (1980).
5. Ibid, p. 127.
6. Bard, A. J. and Faulkner, L. R.: "Electrochemical Methods, Fundamentals and Applications", 1980, John Wiley and Sons, pp. 249-257.

TABLE 1. SUMMARY OF EQUATIONS USED FOR CHRONOPOTENTIOMETRIC MODELS

Model	Equation(s)
IV	$E = 1.294 + \frac{RT}{F} \ln \left[\frac{1-x^{1/2}}{x^{1/2}} \right] - iR_o$
IV A	$E = 1.47 + \frac{RT}{F} \ln \left[\frac{1-(x+1-0.0726)^{1/2}}{(x+1-0.0726)^{1/2}} \right] - iR_o \quad x < 0.0726$
	$E = 1.294 + \frac{RT}{F} \ln \left[\frac{1-(x-0.0726)^{1/2}}{(x-0.0726)^{1/2}} \right] - iR_o \quad x \geq 0.0726$
IV B	$E = 1.47 + \frac{RT}{F} \ln \left[\frac{1-(x+1-0.0310)^{1/2}}{(x+1-0.0310)^{1/2}} \right] - iR_o \quad x < 0.0310$
	$E = 1.294 + \frac{RT}{F} \ln \left[\frac{1-x^{1/2}}{x^{1/2}} \right] - iR_o \quad x \geq 0.0310$
IV C	$E = 1.47 + \frac{RT}{F} \ln \left[\frac{1-(x+1-0.0594)^{1/2}}{(x+1-0.0594)^{1/2}} \right] - iR_o \quad x < 0.0594$
	$E = 1.294 + \left[\frac{RT}{F} \ln \frac{1-(x+0.0594)^{1/2}}{(x+0.0594)^{1/2}} \right] - iR_o \quad x \geq 0.0594$

TABLE 2. SUMMARY OF ERRORS FOR CHRONOPOTENTIOMETRIC MODELS

Model	0 - 100%		0 - 40%		0 - 25%	
	Std Dev mV	Avg Dev mV	Std Dev mV	Avg Dev mV	Std Dev mV	Avg Dev mV
IV	13.4	9.4	16.3	12.7	19.6	15.4
IV A	18.5	16.0	24.9	22.8	26.8	23.9
IV B	14.1	9.8	16.9	12.3	20.6	15.5
IV C	15.9	10.3	11.7	10.0	12.9	10.6

TABLE 3. SUMMARY OF EQUATIONS USED FOR THERMODYNAMIC MODELS

Model

Equation

all models based on

$$E = 1.294 + \frac{RT}{F} \ln \left[\frac{1-x}{x} \right] + K \frac{RT}{F} (2x-1) - iR_o$$

II

$$K = 0.789$$

II A

$$K = 0.014$$

$$x < 0.15$$

$$K = 1.374$$

$$0.15 \leq x \leq 0.40$$

$$K = 0.918$$

$$x > 0.40$$

II B

$$K = -0.326$$

$$x \leq 0.10$$

$$K = 1.116$$

$$0.10 < x < 0.40$$

$$K = 0.918$$

$$x \geq 0.40$$

TABLE 4. SUMMARY OF ERRORS FOR THERMODYNAMIC MODELS

Model	0 - 100%		0 - 40%		0 - 25%	
	Std Dev mV	Avg Dev mV	Std Dev mV	Avg Dev mV	Std Dev mV	Avg Dev mV
II	8.5	4.7	11.2	8.7	13.7	10.8
II A	7.1	3.7	8.7	5.3	12.0	7.6
II B	6.8	3.7	8.0	5.4	10.2	7.6

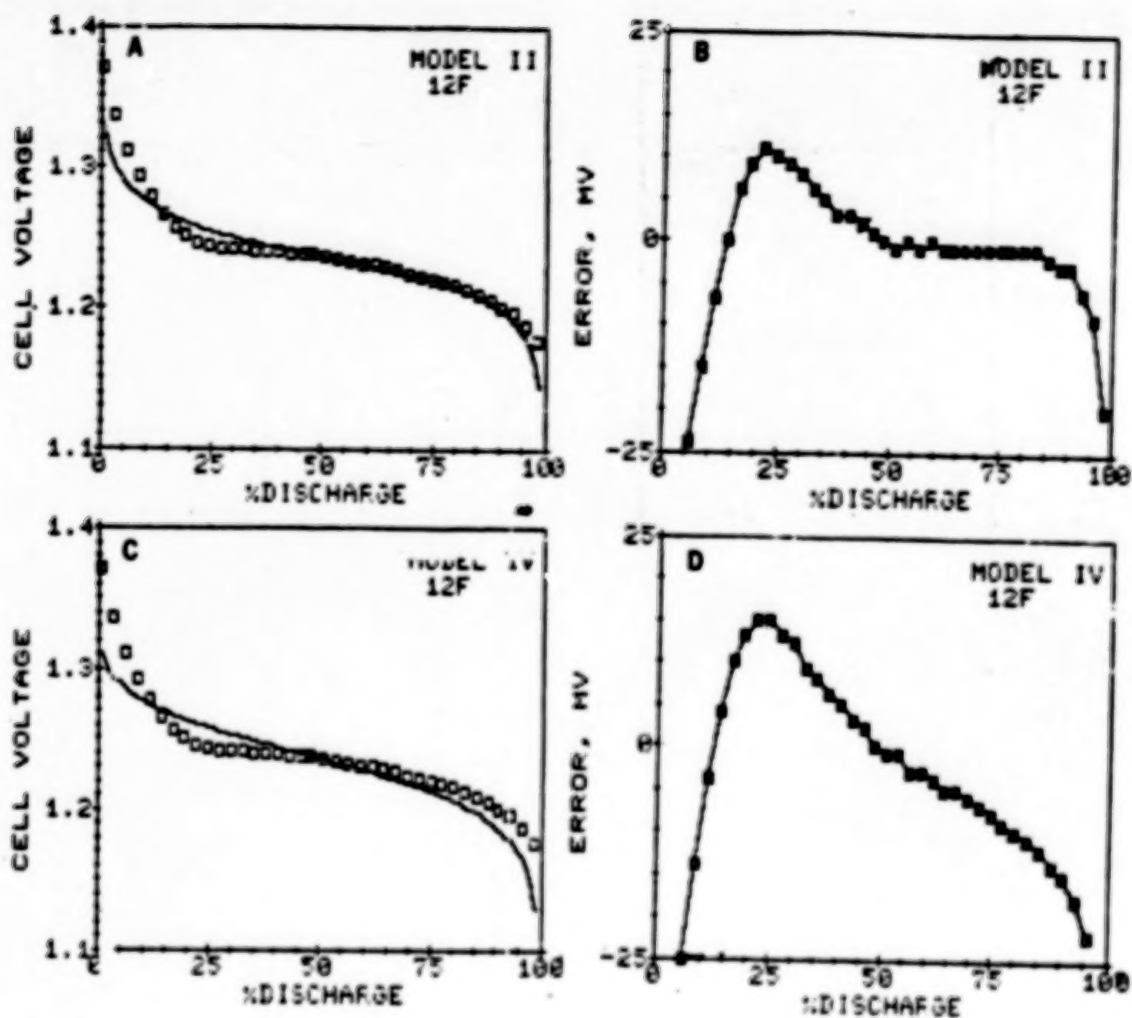


Figure 1. Typical results from previous study. Curves A,B: thermodynamic model II; curves C,D: chronopotentiometric model IV. Curves A and C are discharge curves; squares represent experimental data. Curves B and D are corresponding error curves.

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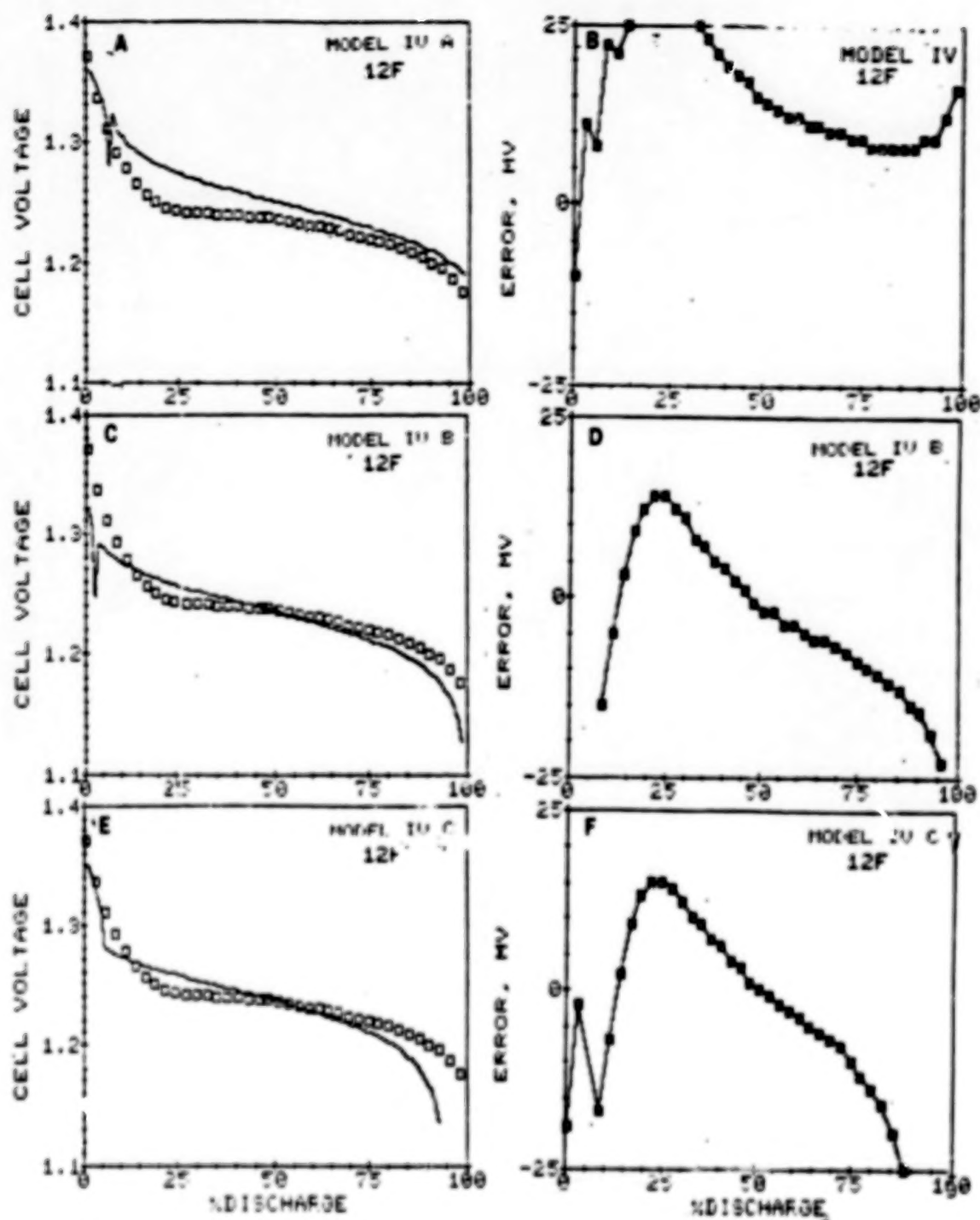


Figure 2.

Typical Results for chronopotentiometric models. Curves A,B: model IV A; curves C,D: model IV B; curves E,F: model IV C. Curves A, C and E are discharge curves; squares represent experimental data. Curves B, D and F are corresponding error curves.

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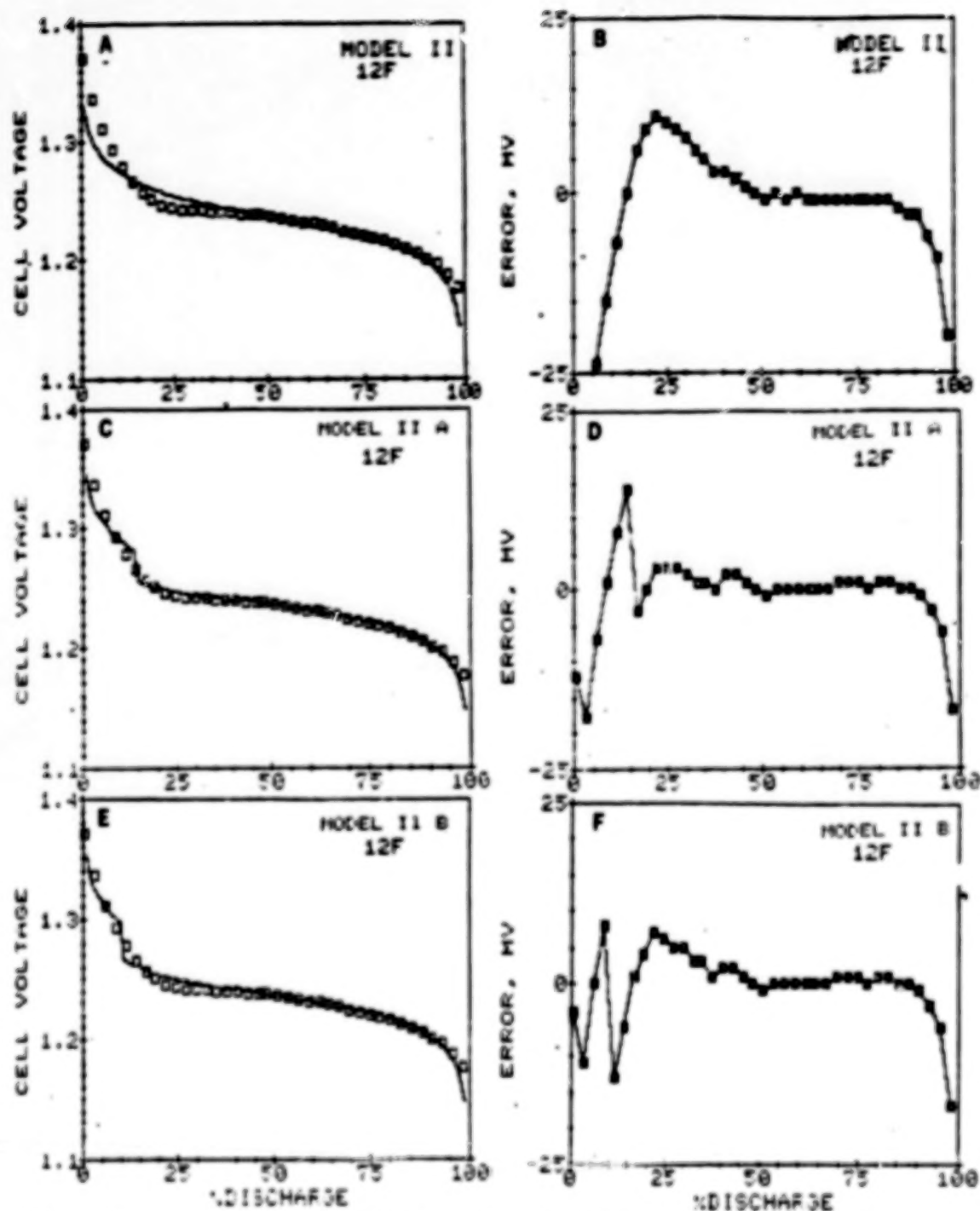


Figure 3.

Typical results for thermodynamic models. Curves A,B: model II; curves C,D: model II A; curves E,F: model II B. Curves A,C and E are discharge curves; squares represent experimental data. Curves B, D and F are corresponding error curves.

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MODELING A Li/SOCl_2 BATTERY FOR DESIGN PURPOSES

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Anatech, Inc.

INTRODUCTION

The Navy has used computer modeling to help in the development of various batteries. Some such efforts were the Mg/AgCl seawater battery, the Li/Cl_2 battery and the Al/AgO battery. Currently, the Navy is developing, under contract with GTE, a 180 KW Li/SOCl_2 battery for propulsion applications that utilizes a flowing electrolyte design. The development of a new battery requires considerable experimentation and involves the construction and testing of full size prototypes. In addition, the operating conditions for such batteries often encompasses a wide range of operating conditions such as temperature, current densities, and varying electrolyte compositions. Because of these factors, the expense involved in building and testing prototype batteries is high and computer modeling can help reduce the development costs. The aim of the present work is to develop a generalized code applicable to many different electrochemical systems and geometric designs.

Figure - 1

The code is to be set up so that physical property data such as thermal conductivity, viscosity, density, and configuration (e.g. physical dimensions) are the input data. Thus, by changing these parameters many different battery configurations can be handled. The outputs, as a function of time and space, are voltage, current, temperature, pressure, velocity, and species concentration.

Figure - 2

In certain high-rate batteries, internal heat generation is needed to maintain battery operation at the temperature level for optimal electrochemical operation. However, this same heat generation is disastrous if internal temperatures go too high and hazardous chemical reactions are initiated. Rapid deterioration of materials in the corrosive electrolyte is also more likely to occur at higher temperatures. If the high-rate flowing electrolyte battery development program is to be successful, it is necessary to solve the heat management problem and computer modeling will greatly aid this effort.

APPROACH

Figure - 3

Batteries are highly coupled systems as follows: 1) The temperature field is a function of discharge rate, chemical reactions, electrochemical reactions, material properties, and physical layout; 2) The current density field is a function of species concentration, temperature, material properties, and the history of the discharge cycle; 3) Material properties are functions of temperature and species concentration; and 4) Species concentration are functions of reaction rate history, electric field, and fluid flow conditions. Many computer codes using techniques such as finite differences, finite element, electrical network analogy, and polynomial collocation are available to solve such complex coupled equations. For this effort, a finite element code call NACHOS was selected as the starting point. This code was originally designed for the analysis of two-dimensional, viscous, incompressible fluid flow problems including heat transfer effects. No attempt will be made to go into the details about the mathematics of the finite element method. Instead, to illustrate the method, an example will be described and while discussing the example, pertinent points about the finite element method will be made. To gain experience with the code on the laboratory 6500 CDC computer and to show the effect of massive end plates on a cell test fixture, the following situation was modeled.

EXPERIMENTAL

Figure - 4

The test fixture is cylindrical in shape (13 cm in diameter by 8.6 cm high). Most of the thickness is in the end plates. A single cell electrode assembly consisting of a Li anode (0.02 cm), a carbon cathode (0.028 cm), and a separator (0.008 cm), is placed between the two end pieces. An O ring electrically insulates the end pieces from each other and contains the electrolyte. There is a center inlet port and an outer outlet port. Because of symmetry considerations, only a portion of the fixture is shown and used in the simulation. The y direction is the axial dimension and the x direction is the radial dimension of the fixture. The $x=0$ axis is the center line of the cell.

The first step in the modeling process is to draw what you want to model and it is not always possible to model the situation as it physically is. For example, the outlet port on the test fixture is actually six channels connected together to form a manifold system. For this modeling exercise the six channels had to be represented by one channel. The next step is to subdivide the geometric model into an interconnecting set of elements by placing a network of nodal points on the model drawing.

Figure - 5

In the NACHOS code each nodal point represents values of temperature, pressure, and velocity. The value of these variables at the nodal points are the unknowns that have to be determined. Various polynomial approximations (quadratic and linear) to the solutions as defined independently over each element are used.

Figure - 6

After the nodal points have been defined in terms of the actual cell fixture, the code then draws in the element mesh and assigns each element a number. In this example, because of the vast differences in end plate thickness (8.6 cm) and cell component thickness (0.05 cm), only a single dark line is seen in the center region and critical analysis does not appear possible. However, the code permits this region to be expanded for examination in greater detail. The nodal mesh for this cell component area can be seen in

Figure - 7 and Figure - 8

In these figures can be seen the element mesh and associated element numbers for the cell component region. The cathode is represented by elements 23, 24, 25, and 26, plus the two rows directly above them. The anode is the top three rows directly above the cathode. The center three rows of elements are the separator region. Elements in columns 22 and 27 are the inlet and outlet channels and the elements in column 28 are the O ring.

One of the advantages of the finite element method is that the elements do not have to be equal in size, shape, or area (triangular, circular, arcs, and irregularly-shaped polyhedral are permitted). They do, however, have to be appropriately joined at the nodal points. It is sometimes useful to use small element sizes in regions where the more interesting changes are taking place and larger elements where less interesting changes are occurring. Another advantage of the finite element method is that at a boundary between two regions (e.g. anode-electrolyte) the polynomial solution is continuous whereas in other methods the solution is discontinuous across such boundaries.

Work on the code has just started and all of the desired features have not been incorporated into it. For instance, in this work the carbon cathode and separator are not treated as porous media. The electrolyte channel in the separator area is considered to be open with electrolyte moving freely through the region. The present simulation is a transient free-convection one, but steady state, forced and mixed convection situations can also be modeled. The simulation which follows was based on a current density of 150 ma/cm², a flow rate of 2 cc/sec. and a polarization value of 0.2 volt, distributed between the anode (0.05V) and the cathode (0.15V). The anode polarization was considered to be a line source of heat along the anode-electrolyte interface. The cathode polarization was considered to be a

volumetric heat source distributed throughout the volume of the cathode. For the present calculation, the entropy contribution and the corrosion heat were not considered but later efforts will include these contributions to the heat. Flow was from the center inlet to the outer edges of the test fixture. In the next five figures, isothermal plots after 4, 20, and 472 seconds can be seen.

Figure - 9

Figure - 10

Figure - 11

Figure - 12

Figure - 13

The heat flow is perpendicular to the plotted isotherms and one can see how it spreads out from the center cell component region. The heat also builds up in the center of the test fixture, mainly in the inlet region. Values for the isotherms are given in the figure and increase in value as the cell component region is approached. The enlarged cell component isotherm lines connect with the isotherm lines in the end plate region.

From this analysis, the temperature increase is approximately 1.2°C whereas calculations using the same input parameters but without the massive end plate show temperature increases of 20°C . Therefore, it is clear that the massive end plates take away considerable quantities of heat.

The code also provides for plotting the pressure and velocity variables in a manner similar to the isotherm plots. One very useful plot is the time-history plot and any variable, temperature, pressure, and velocity for any nodal point can be plotted as a function of time. The final version of the code will also plot voltage and current as a function of time.

Figure - 14

Figure - 15

CONCLUSIONS

NSWC is developing a computer code that can be applied to any electrochemical system or battery design. It uses the finite element approach and utilizes NACHOS as the basic code.

Figure - 16

The code at the present time can do the following:

1. Two-dimensional or axi-symmetric geometry
2. Heat transfer by conduction and convection (free or forced)

3. Internal current flow by circuit analogy
4. Voltage and heat generation due to electrochemical reactions as a function of internal temperature and geometry
5. Automatic plotting of temperature fields, pressure fields, and flow fields on the cell outline
6. Time-history plots of temperature, pressure, velocity, voltage, and current.

By 1984 all of the various field equations will be incorporated and the code will be ready for use.

**MODELING A LI/SOCl₂ BATTERY
FOR
DESIGN PURPOSES**

**DR. D.W. ERNST
MR. D.L. WARBURTON
NSWC**

**DR. A.S. KUSHNER
ANATECH INC.**

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183

APPROACH TO MODELING

OUTPUT

FUNCTION OF SPACE AND TIME

- VOLTAGE
- CURRENT
- TEMPERATURE
- SPECIES CONCENTRATION
- PRESSURE
- VELOCITY

INPUT

- SPATIAL RELATIONSHIP OF CELL BATTERY COMPONENTS
- MATERIAL PROPERTIES
 - THERMAL CONDUCTIVITY
 - ELECTRICAL RESISTIVITY
 - SPECIFIC HEAT
 - DENSITY
 - VISCOSITY
 - ELECTROCHEMICAL POTENTIALS
- BOUNDARY CONDITIONS
 - TEMPERATURE
 - HEAT FLUX
 - PRESSURE
 - EXTERNAL RESISTANCE

FIGURE -1

IN HIGH DISCHARGE RATE BATTERIES INTERNAL HEAT GENERATION IS:

- **ESSENTIAL FOR MAINTAINING BATTERY OPERATION
IN TEMPERATURE REGIME OF OPTIMAL
ELECTROCHEMICAL REACTIONS**
- **DISASTROUS IF IT CAUSES INTERNAL TEMPERATURE
TO RISE TO POINT OF**
 - **DIRECT CHEMICAL REACTION AMONG BATTERY CONSTITUENTS**
 - **SERIOUS DEGRADATION OF MATERIAL STRENGTH
IN CRITICAL COMPONENTS**

FIGURE -2

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185

BATTERIES ARE CHARACTERIZED BY HIGHLY COUPLED SYSTEMS

- **TEMPERATURE FIELD IS FUNCTION OF ELECTRICAL DISCHARGE RATE, CHEMICAL REACTION, ELECTROCHEMICAL REACTION, AND MATERIAL PROPERTIES**
- **CURRENT DENSITY FIELD IS FUNCTION OF SPECIES CONCENTRATION, TEMPERATURE, AND MATERIAL PROPERTIES**
- **MATERIAL PROPERTIES ARE FUNCTIONS OF TEMPERATURE, AND SPECIES CONCENTRATION**
- **SPECIES CONCENTRATION ARE FUNCTIONS OF REACTION RATE HISTORY AND FLUID FLOW CONDITIONS**

FOUR INCH TEST FIXTURE OUTLINE

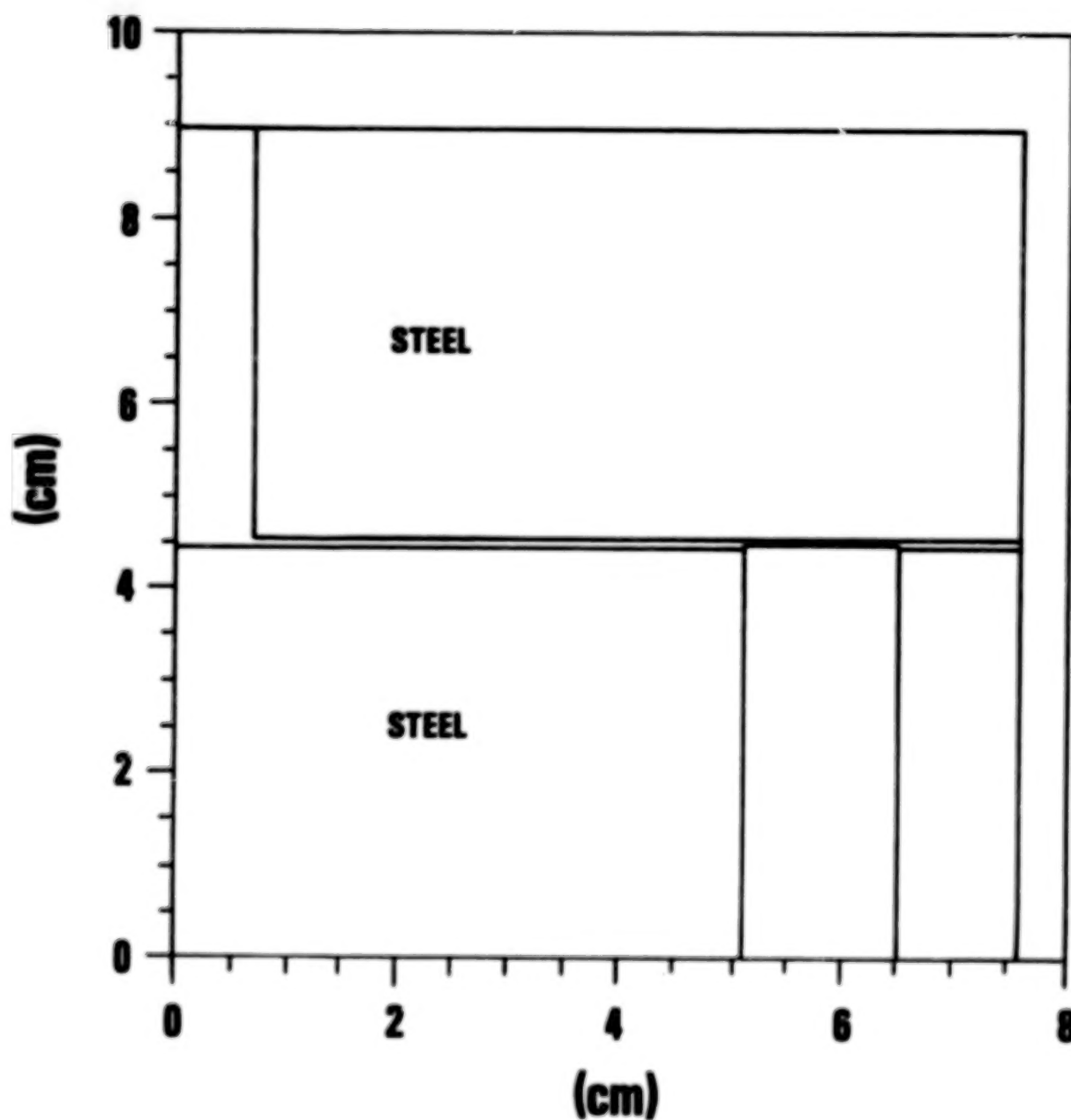


FIGURE -4 MODEL OF TEST FIXTURE

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FOUR INCH TEST FIXTURE

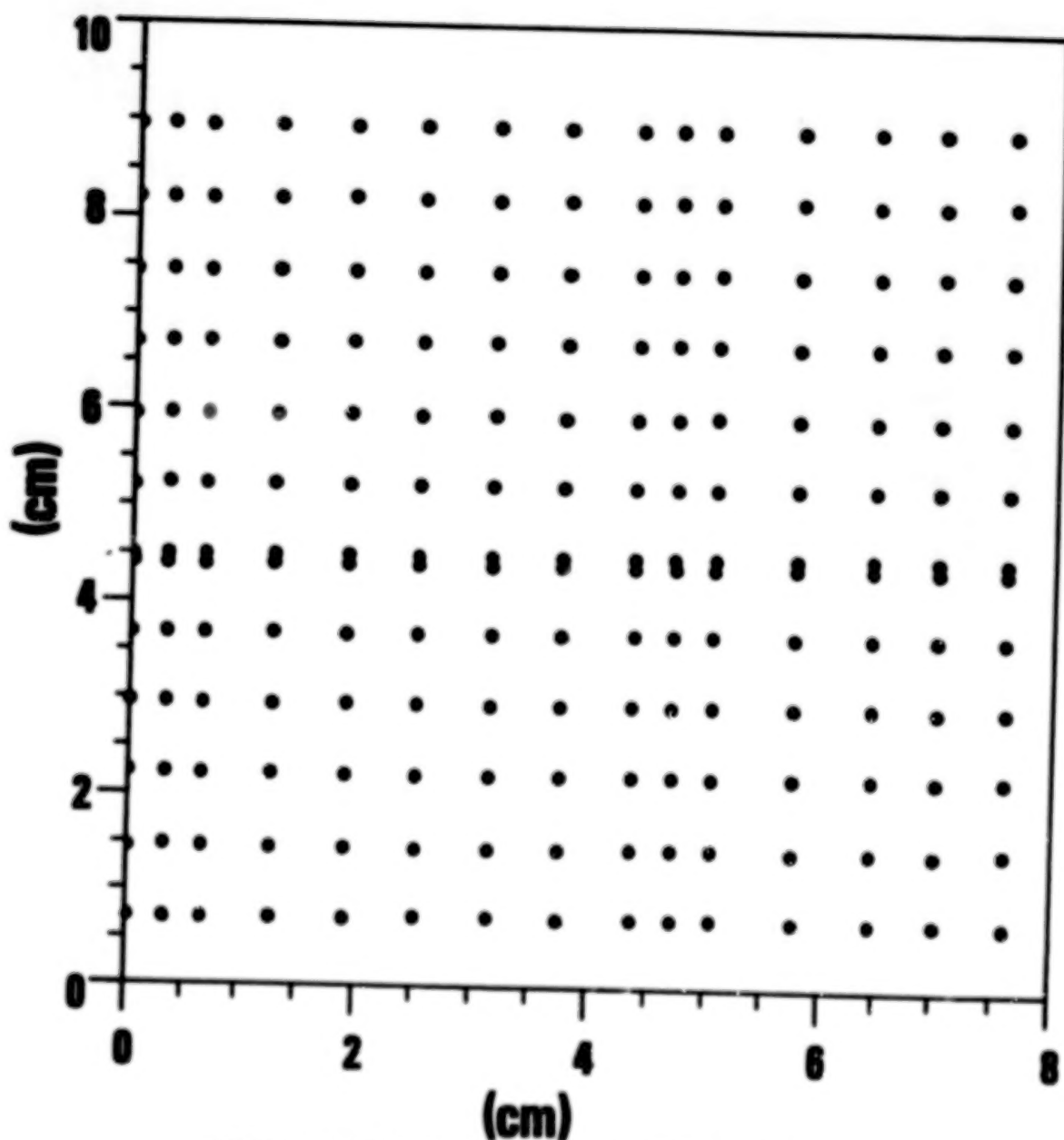


FIGURE -5 NODAL POINTS SUPERIMPOSED ON MODEL

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FOUR INCH TEST FIXTURE

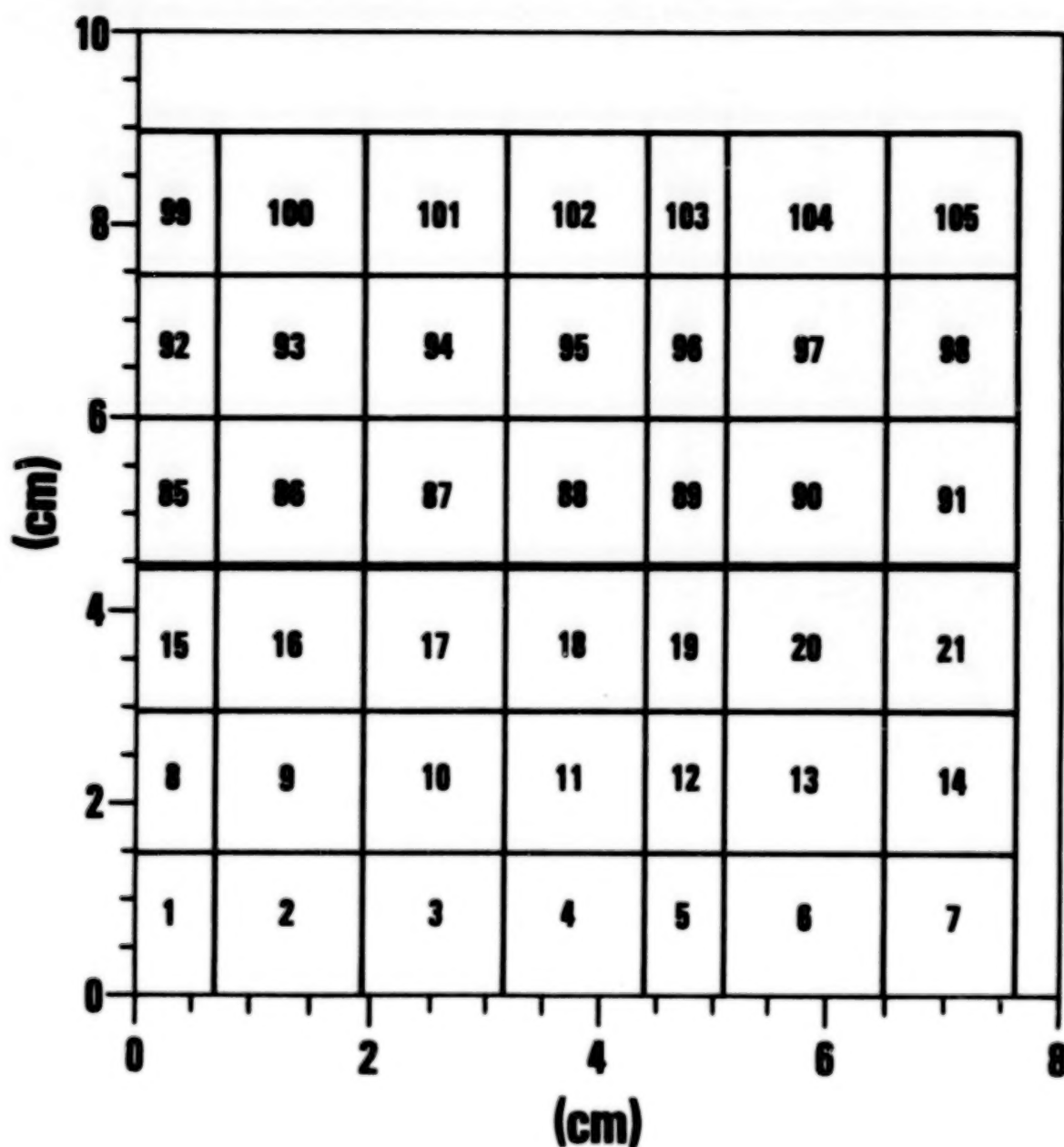


FIGURE -8 ELEMENT MESH DERIVED FROM NODAL POINTS

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FOUR INCH TEST FIXTURE

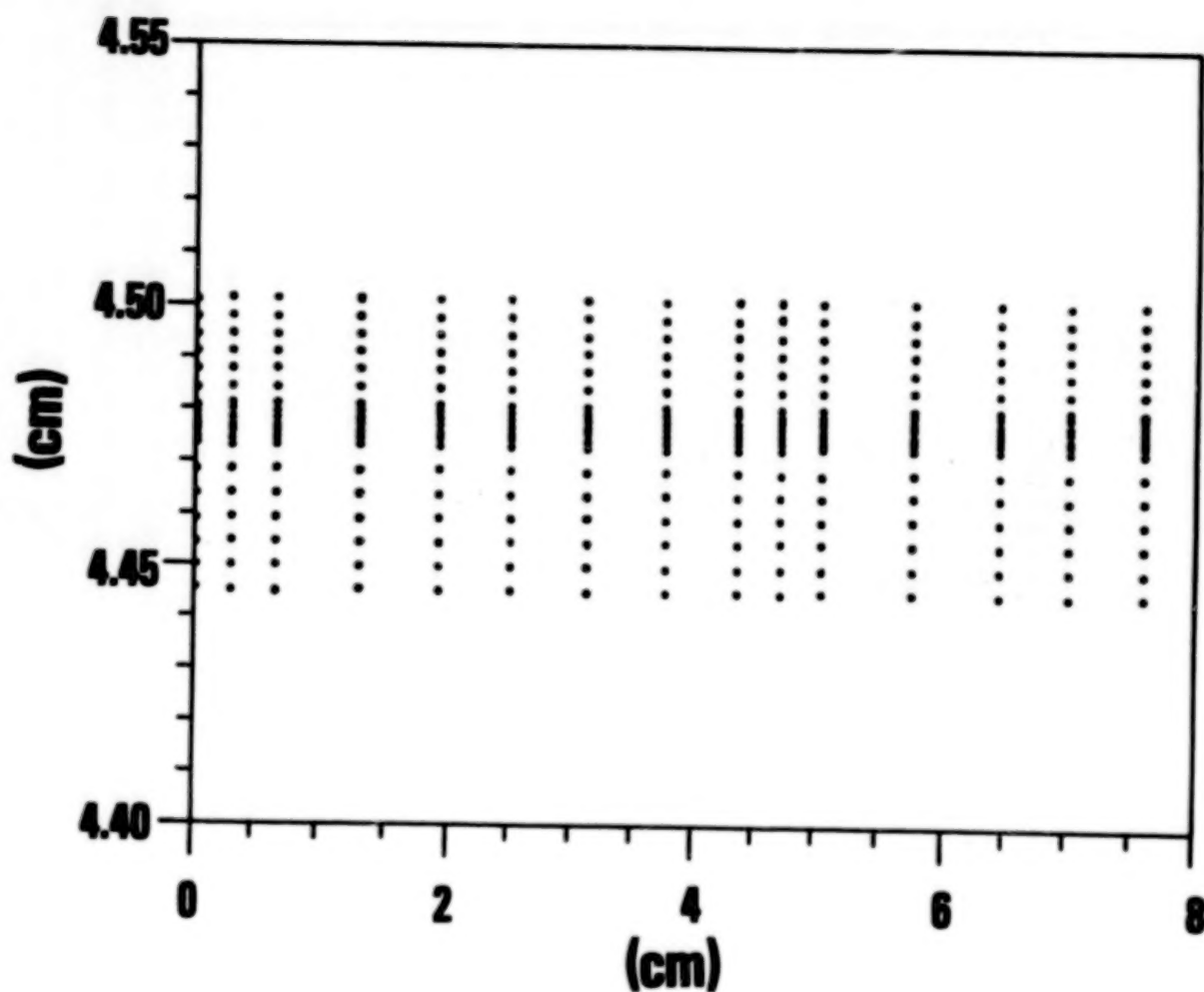


FIGURE -7 NODAL POINTS FOR CELL COMPONENT REGION OF MODEL

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FOUR INCH TEST FIXTURE

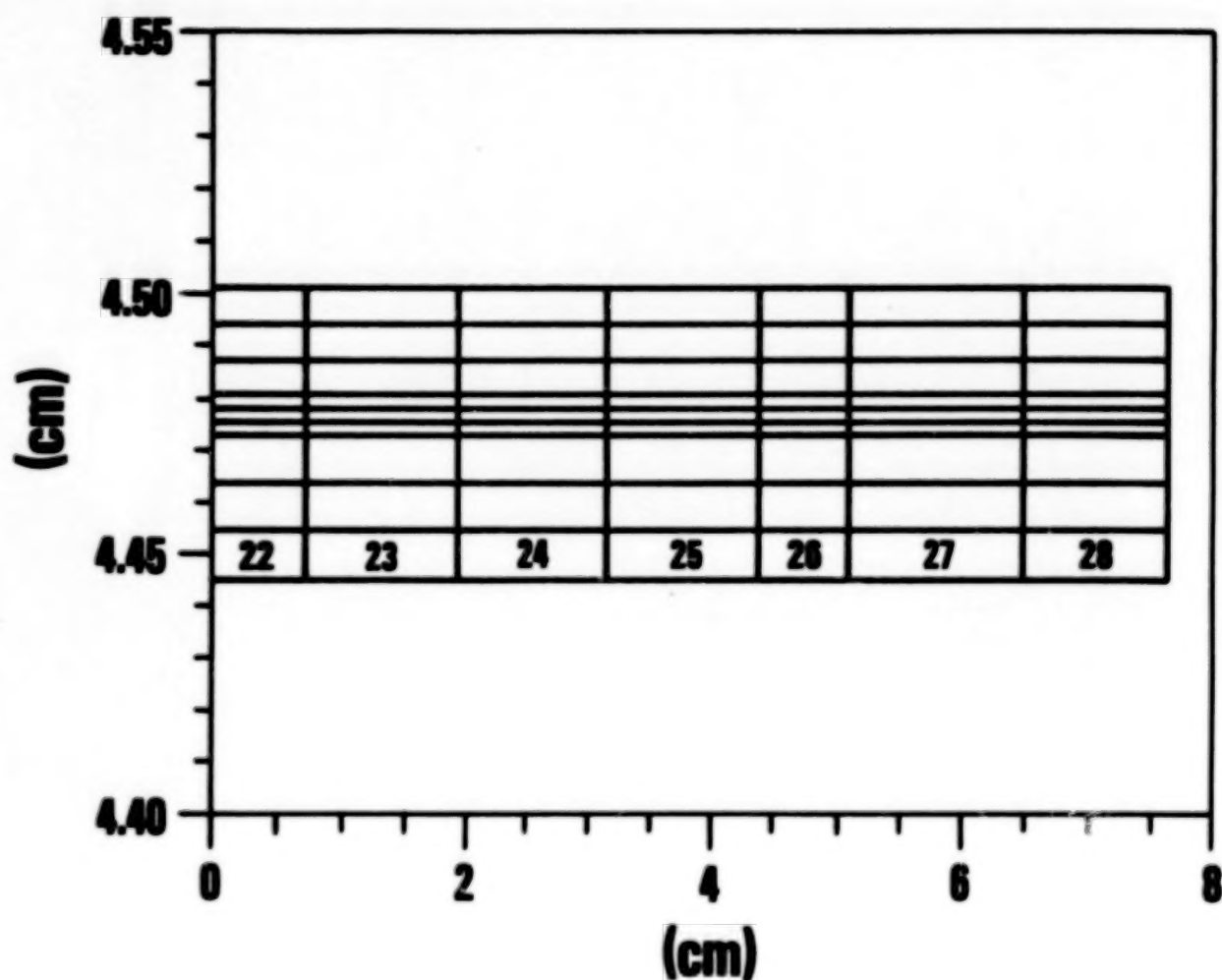


FIGURE -8 ELEMENT MESH FOR CELL COMPONENT REGION

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FOUR INCH FIXTURE (0.2, 0.150, -2.0 28) ISOTHERMS

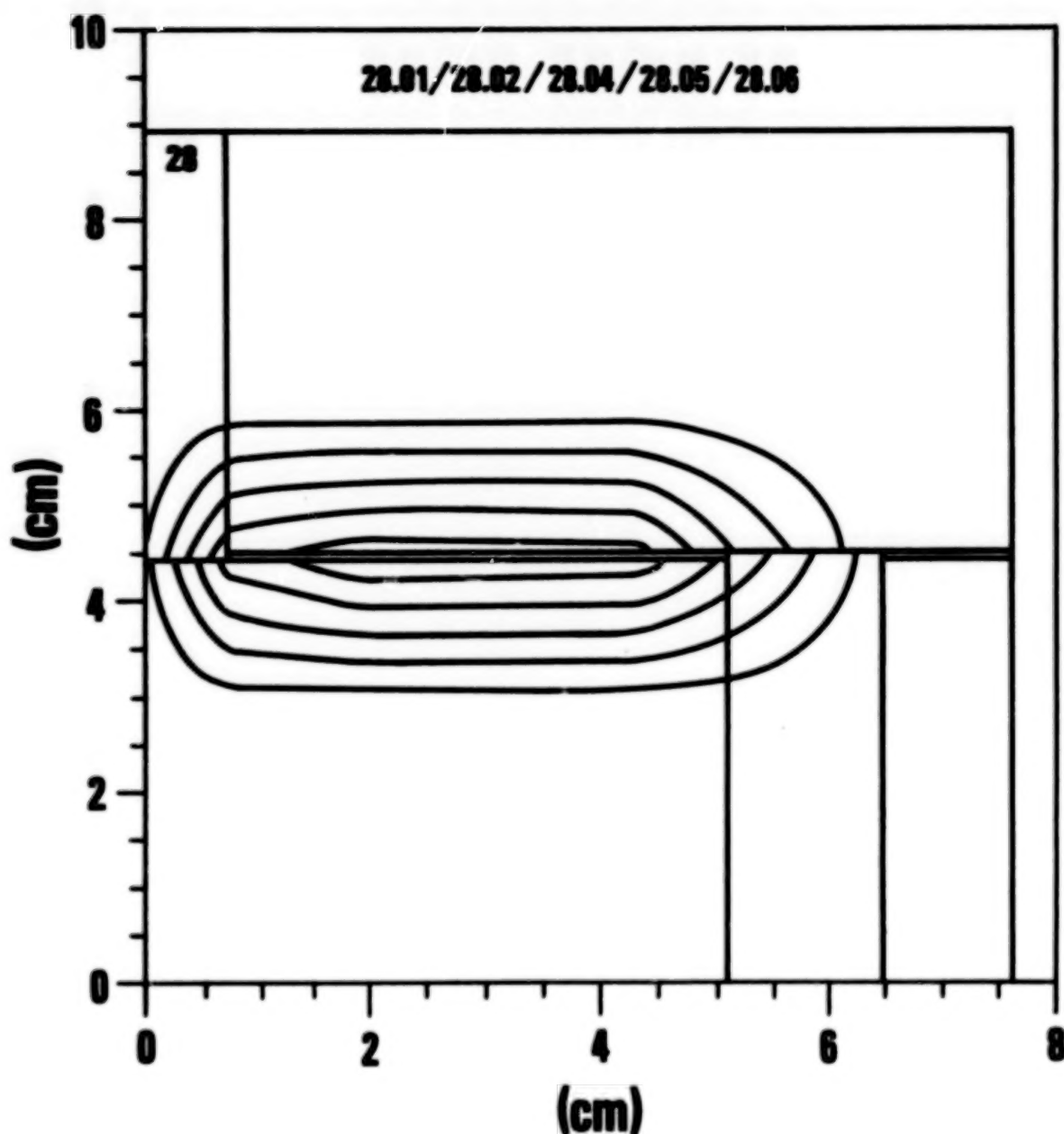


FIGURE -8 PLOT OF ISOTHERMS AFTER 4 SECONDS

BEST DOCUMENT AVAILABLE

FOUR INCH FIXTURE (0.2, 0.150, -2.0 28) ISOTHERMS

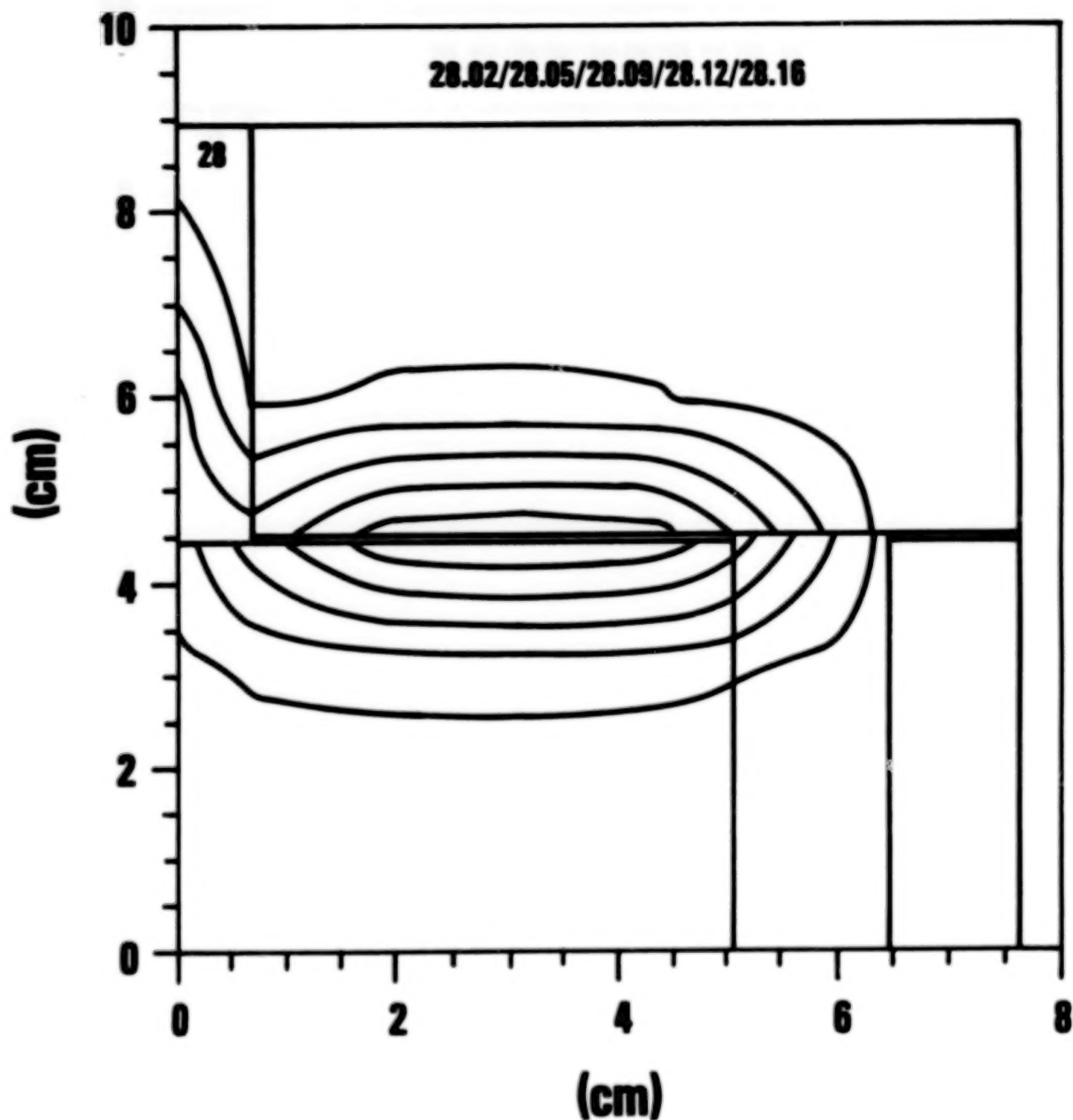


FIGURE -10 PLOT OF ISOTHERMS AFTER 20 SECONDS

BEST DOCUMENT AVAILABLE

FOUR INCH FIXTURE (0.2, 0.150, -2.0 28) ISOTHERMS

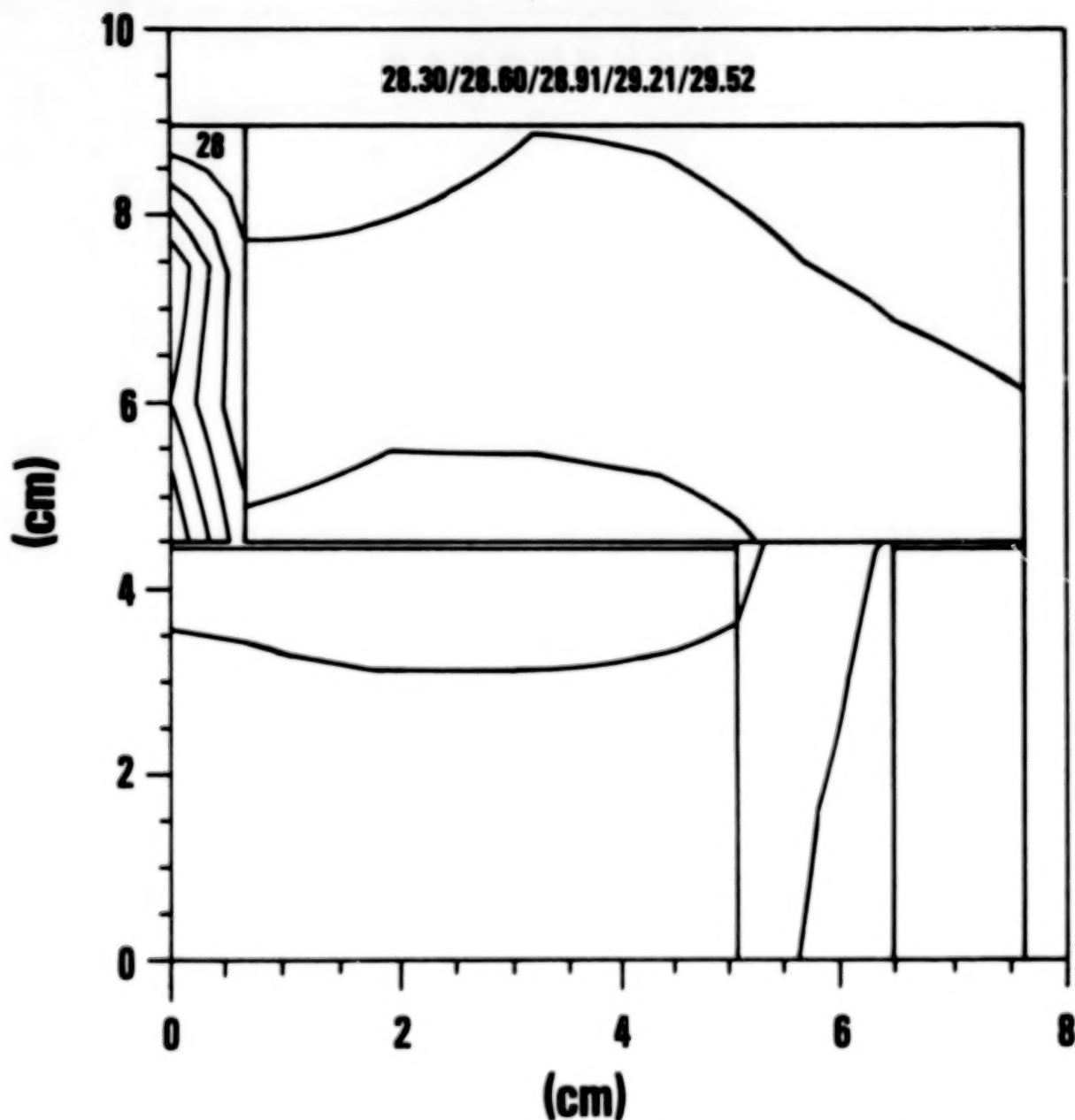


FIGURE - 11 PLOT OF ISOTHERMS AFTER 472 SECONDS

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FOUR INCH FIXTURE (0.2, 0.150, -2.0 28) ISOTHERMS

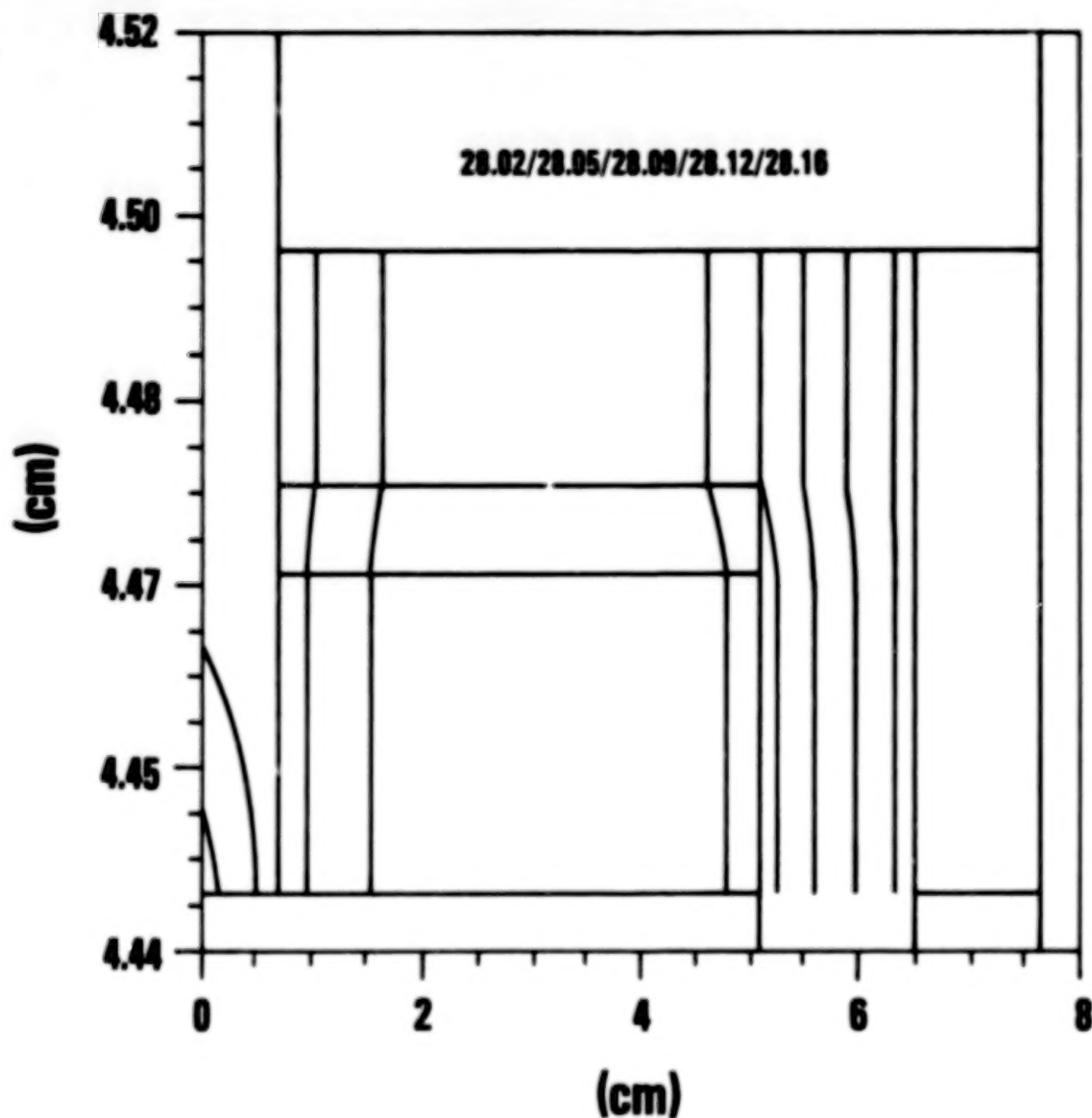


FIGURE - 12 PLOT OF ISOTHERMS AFTER 20 SEC

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FOUR INCH FIXTURE (0.2, 0.150, -2.0 28) ISOTHERMS

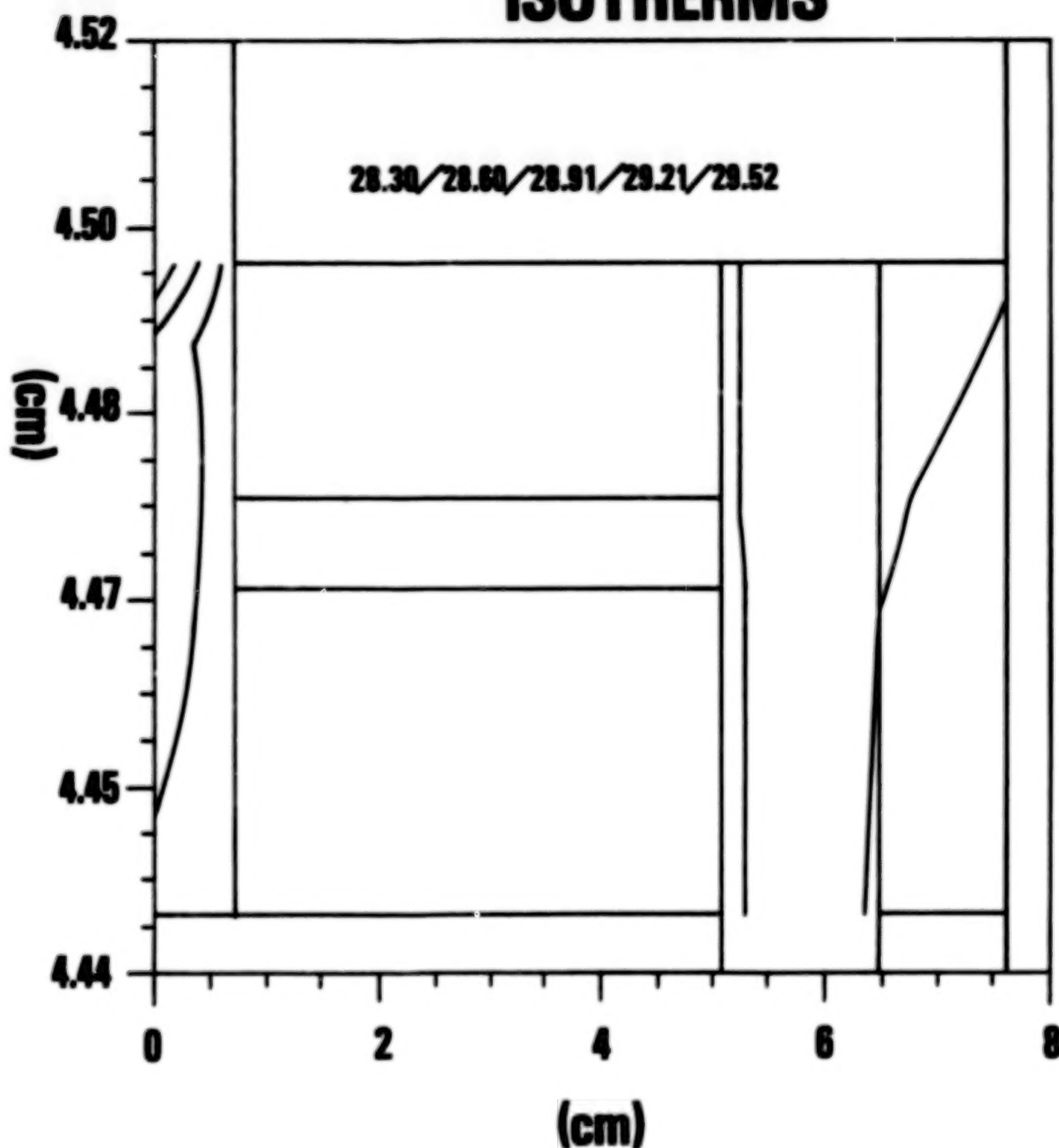


FIGURE -13 PLOT OF ISOTHERMS AFTER 472 SECONDS

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**FOUR INCH TEST FIXTURE (0.2, 0.150, -2.0 28)
ELEMENT = 51 DEGREE OF FREEDOM = 28**

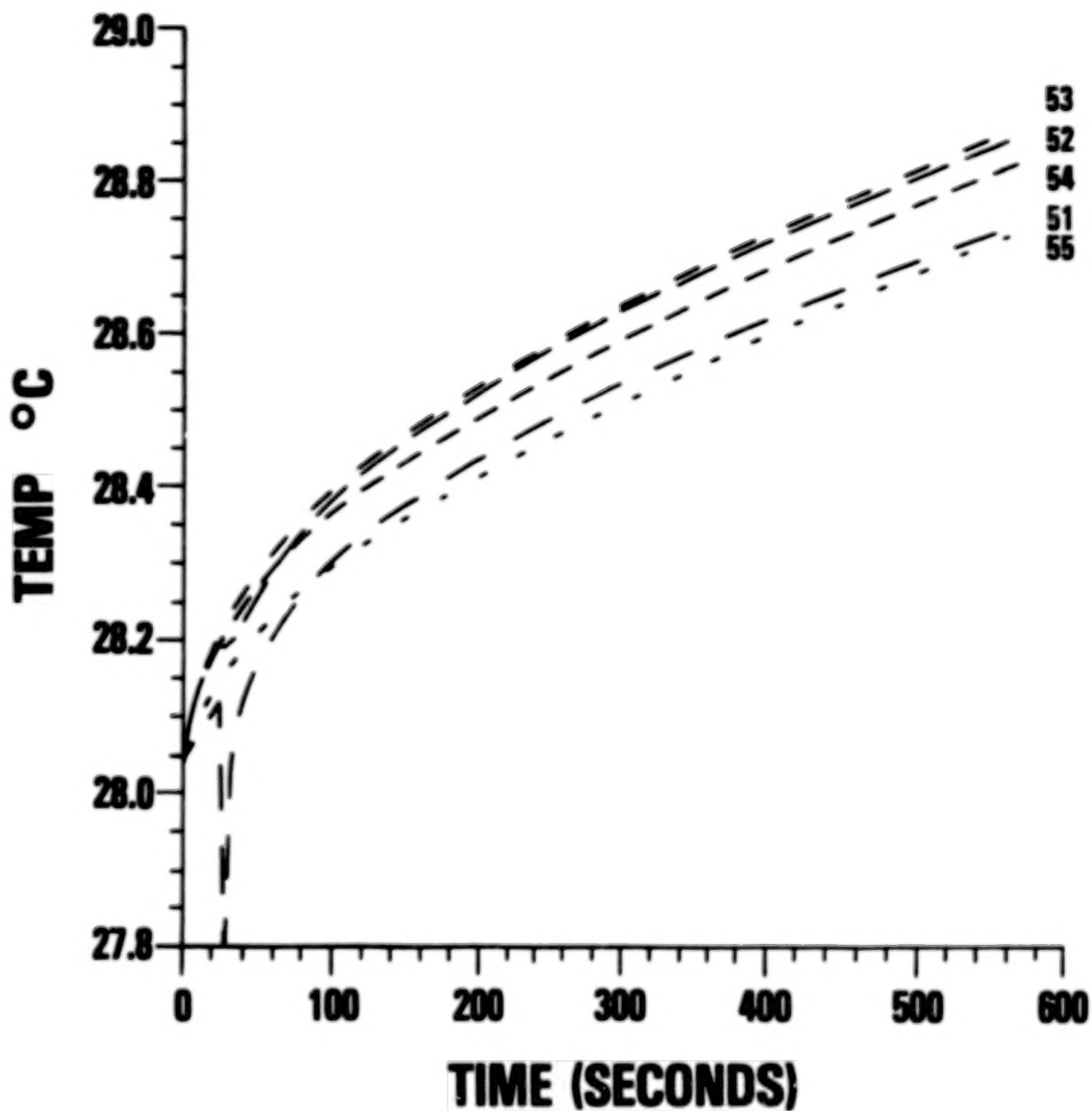


FIGURE -14 TIME-HISTORY PLOT FOR FIVE ELEMENTS

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FOUR INCH TEST FIXTURE (0.2, 0.150, -2.0 28)
ELEMENT = 51 DEGREE OF FREEDOM = 28

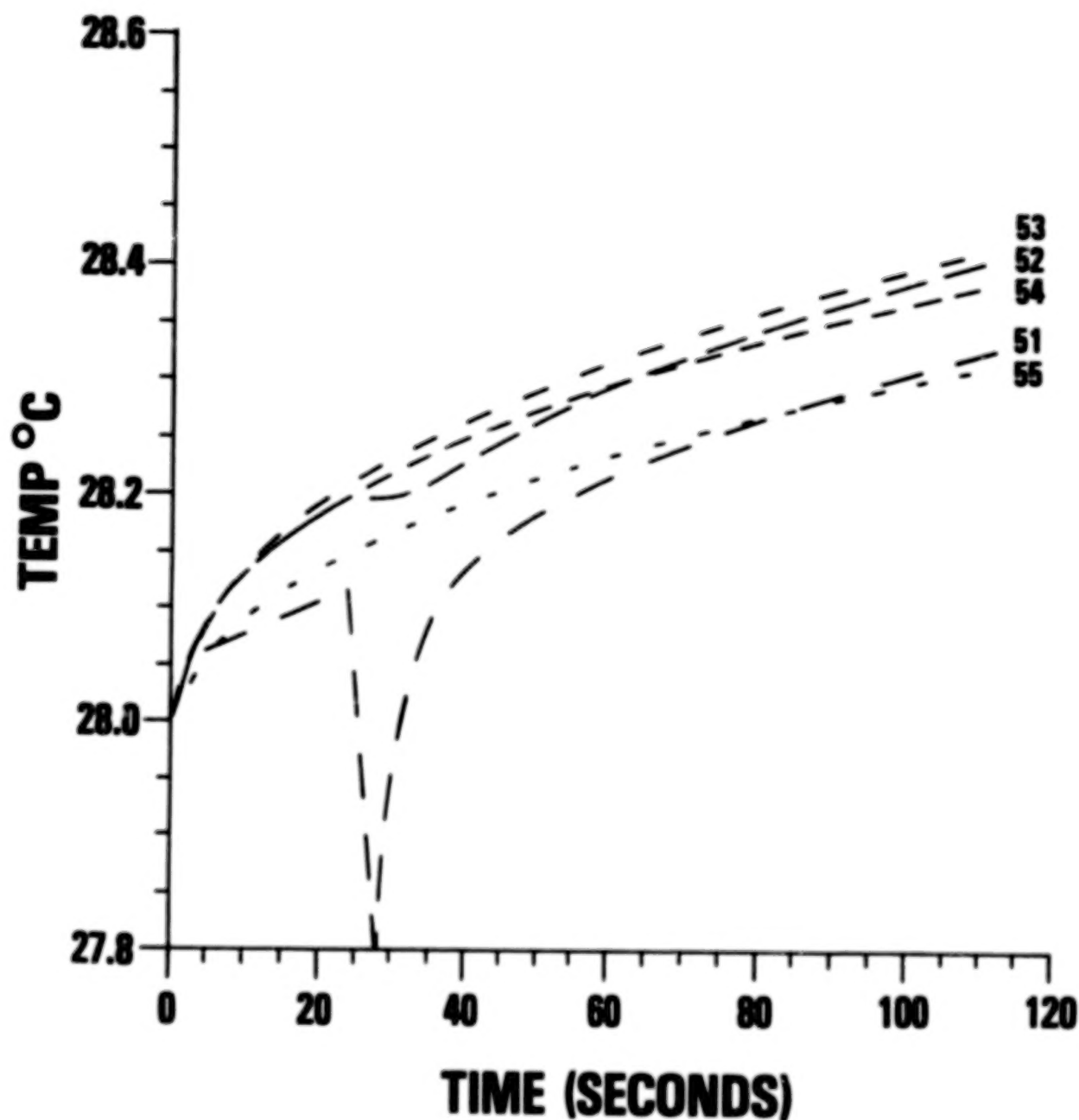


FIGURE -15 TIME-HISTORY PLOT FOR FIVE ELEMENTS

COMPUTER CODE CAPABILITY

PRESENT (FY 82)

- TWO DIMENSIONAL OR AXIS SYMMETRIC GEOMETRY
- HEAT TRANSFER BY CONDUCTION AND CONVECTION (FREE & FORCED)
- INTERNAL CURRENT FLOW BY CIRCUIT ANALOGY
- VOLTAGE AND HEAT GENERATION DUE TO ELECTROCHEMICAL REACTION AS FUNCTIONS OF INTERNAL TEMPERATURE AND GEOMETRY
- AUTOMATIC PLOTTING OF TEMPERATURE FIELDS, PRESSURE FIELDS, AND FLOW FIELDS ON CELL OUTLINE
- TIME HISTORY PLOTS OF CELL VOLTAGE, CELL CURRENT OR TEMPERATURE, PRESSURE AND VELOCITY AT A POINT

FUTURE FY 83

- CONCENTRATION GRADIENTS DUE TO DIFFUSION AND ELECTRIC POTENTIALS
- ELECTRIC FIELD POTENTIAL AND ASSOCIATED CURRENT VECTOR
- COUPLING OF ABOVE WITH TEMPERATURE AND FLUID FLOW SOLUTIONS

OTHER PRESENTATIONS

COMPUTER MODELING OF BATTERIES FROM
NON-LINEAR CIRCUIT ELEMENTS

S. Waaben, J. Federico, and I. Moskowitz, Bell Labs.

Computer Modeling of Batteries from Non-linear Circuit Elements

S. Waaben, J. Federico, and I. Moskowitz

Abstract

Circuit analog models for batteries have previously been composed of resistors, capacitors, and inductors. Such linear circuit models fail to adequately simulate many battery characteristics including state of charge, turn-on transients, recovery from rapid discharge, and gassing effects.

This work introduces a simple non-linear circuit model for battery behavior. It is based on time-dependent features of the well-known PIN charge storage diode, whose behavior is described by equations similar to those associated with electrochemical cells. The circuit simulation computer program ADVICE has been used to predict non-linear responses from a topological description of the battery analog built from ADVICE components. By a reasonable choice of one set of parameters, the circuit accurately simulates a wide spectrum of measured non-linear battery responses to within a few millivolts.

COMPUTER MODELING OF BATTERIES **FROM NON-LINEAR CIRCUIT ELEMENTS**

S. Waaben, J. Federico, I. Moskowitz
BELL LABORATORIES

1. MOTIVATION; WHY NOW

- MEASUREMENTS
- STANDARD COMPUTERIZED CIRCUIT DESIGN TOOLS

2. DEVELOPMENT

- OPEN - CIRCUIT
- CHARGE - DISCHARGE
- μ S PULSE RESPONSE

3. SIMULATIONS NiCd, Pb-ACID

4. SUMMARY

I. MOTIVATION; WHY NOW

- BATTERY ↔ CIRCUIT ELEMENT

- BATTERY: INTERCONNECTION OF
DISCRETE ELECTRONIC PARTS

- MEASUREMENT DIFFICULTIES
OVERCOME: POWER FET, COMPUTER

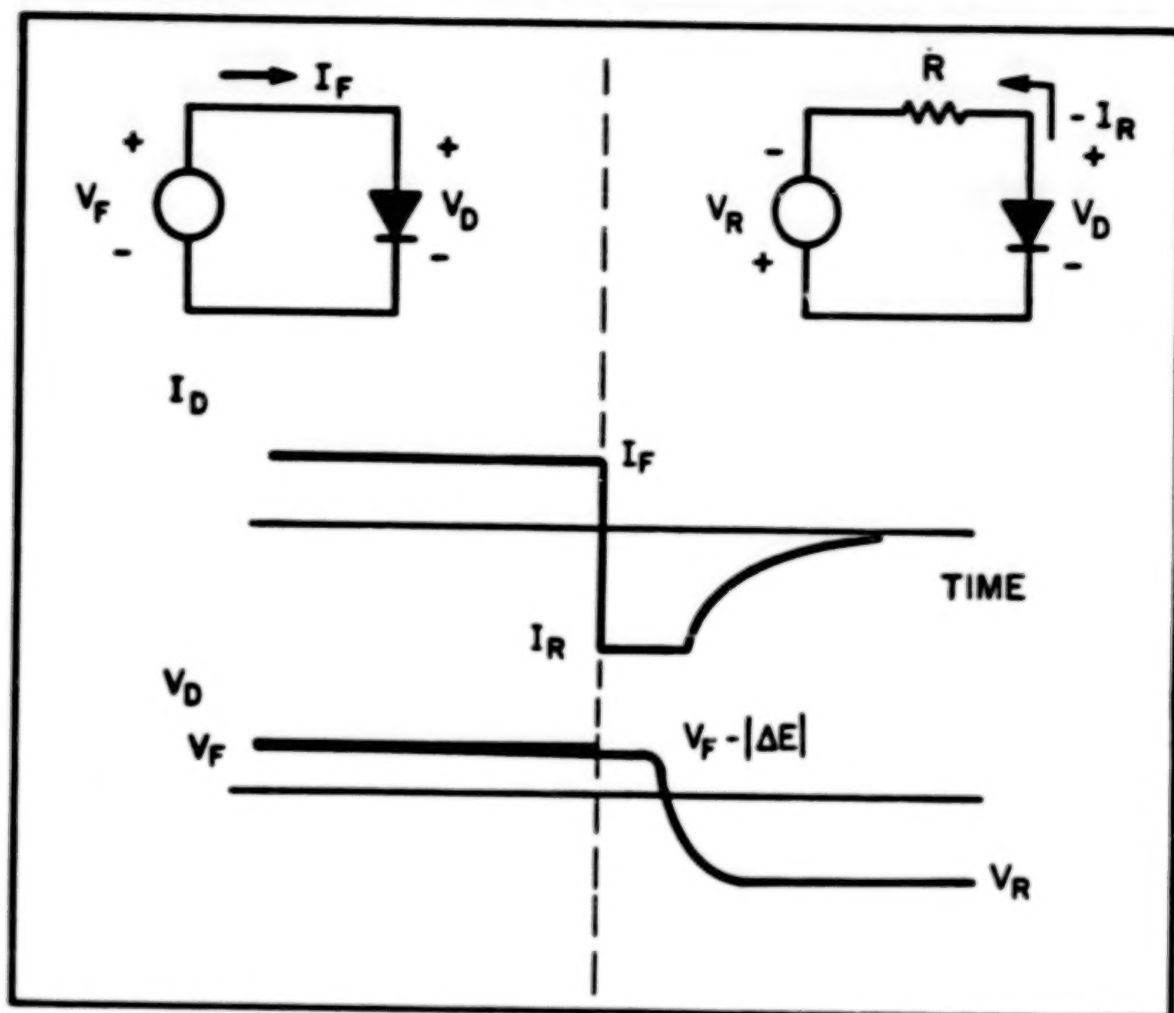
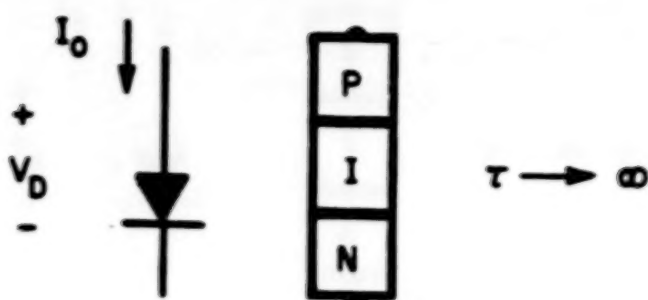
- COMPUTER CIRCUIT ANALYSIS TOOLS



BATTERY MODEL

- NON - LINEAR
- EASILY IMPLEMENTED
- ACCURATE

MODEL:
P-I-N DIODE



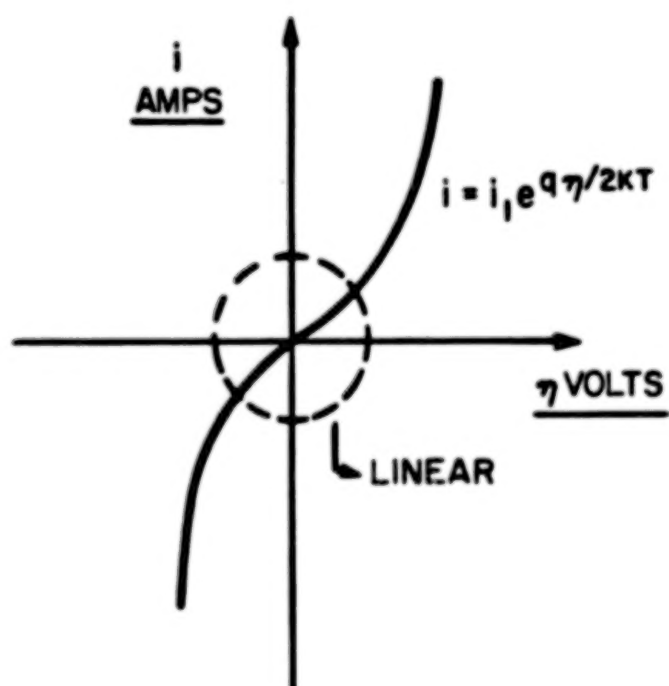
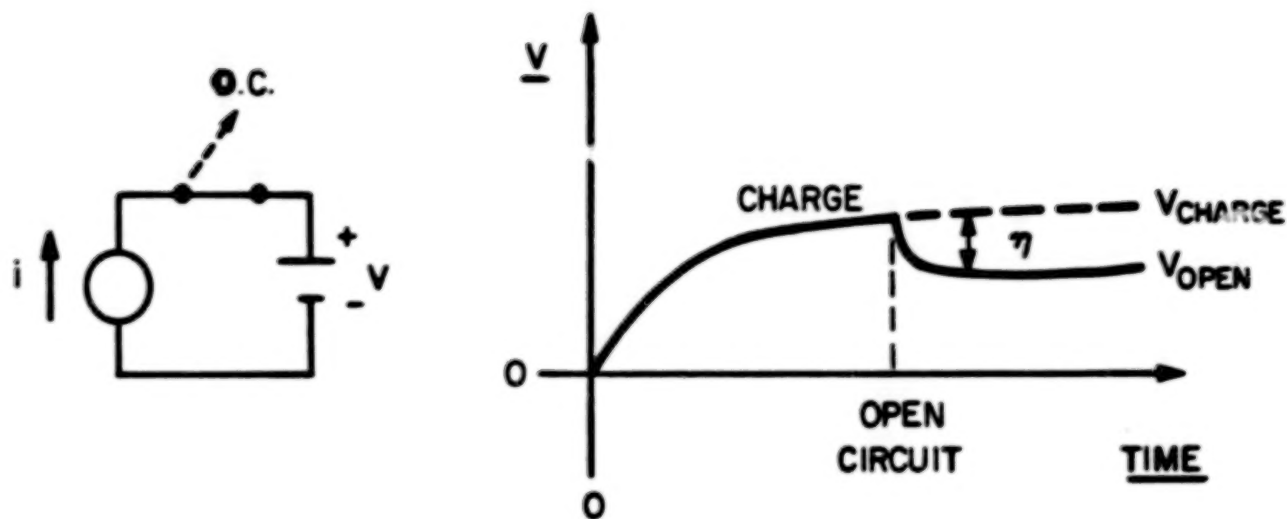
DIODE: $I_D = I_0 e^{qV/KT}, \tau \rightarrow \infty$

BATTERY:

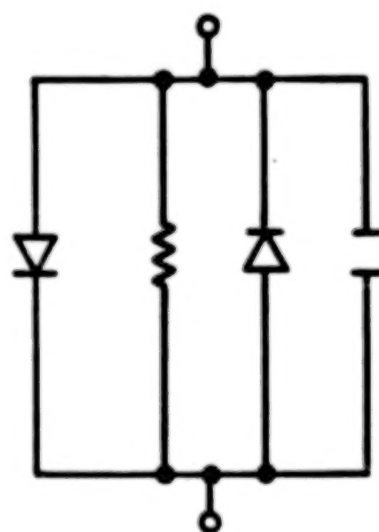
$\frac{I_0}{V} + V \quad I = I_0 e^{qV/2KT}$

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DEVELOPMENT: CHARGE-DISCHARGE 'OVERVOLTAGE' η



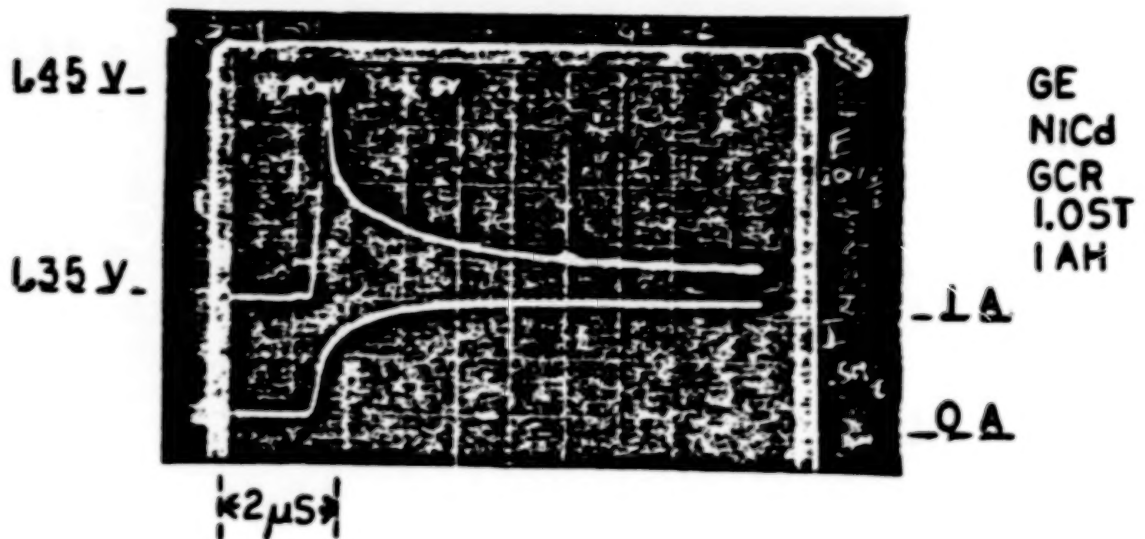
i - η PLOT



OVERVOLTAGE
MODEL

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DEVELOPMENT : μ S RESPONSE

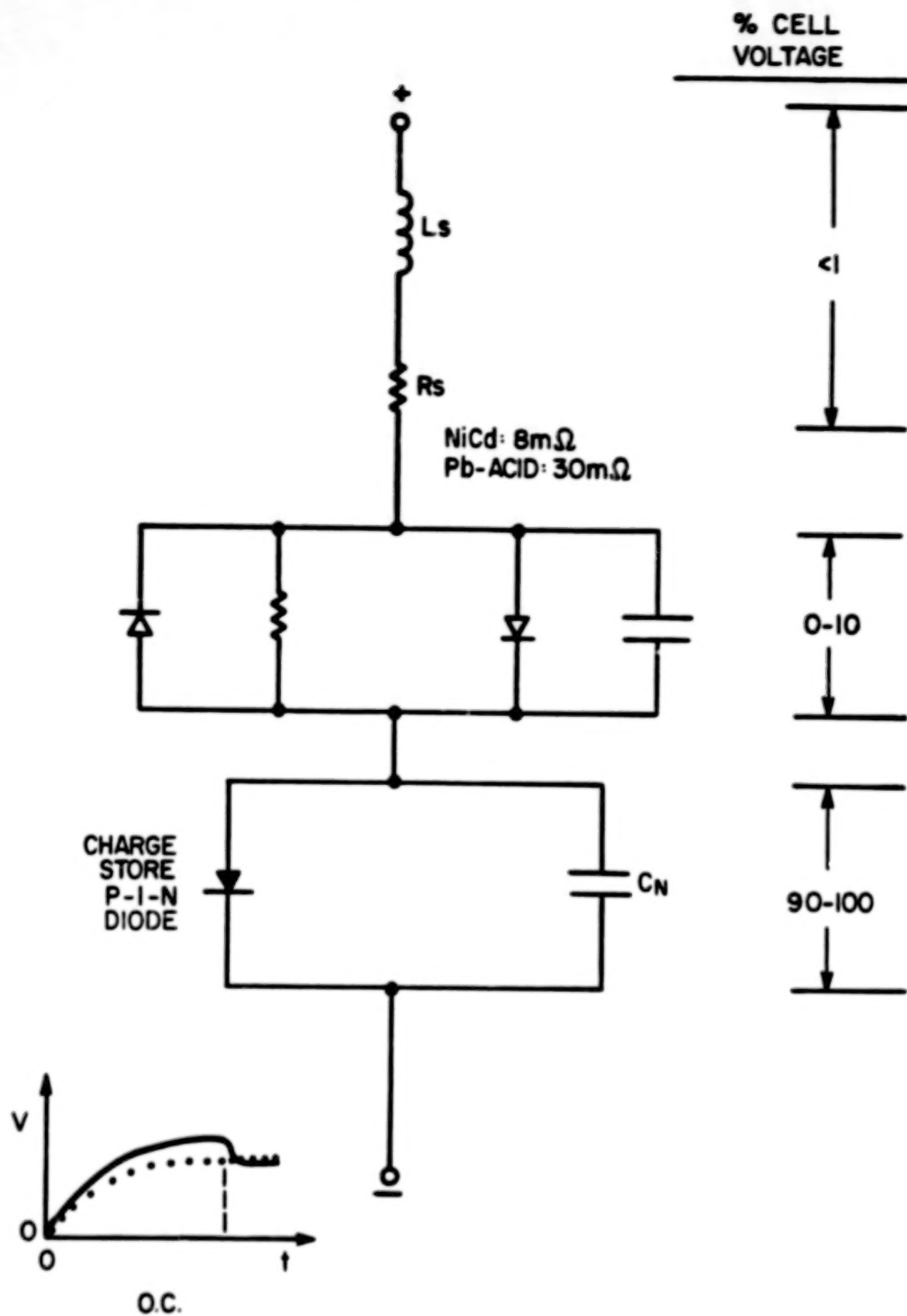


INDUCTOR

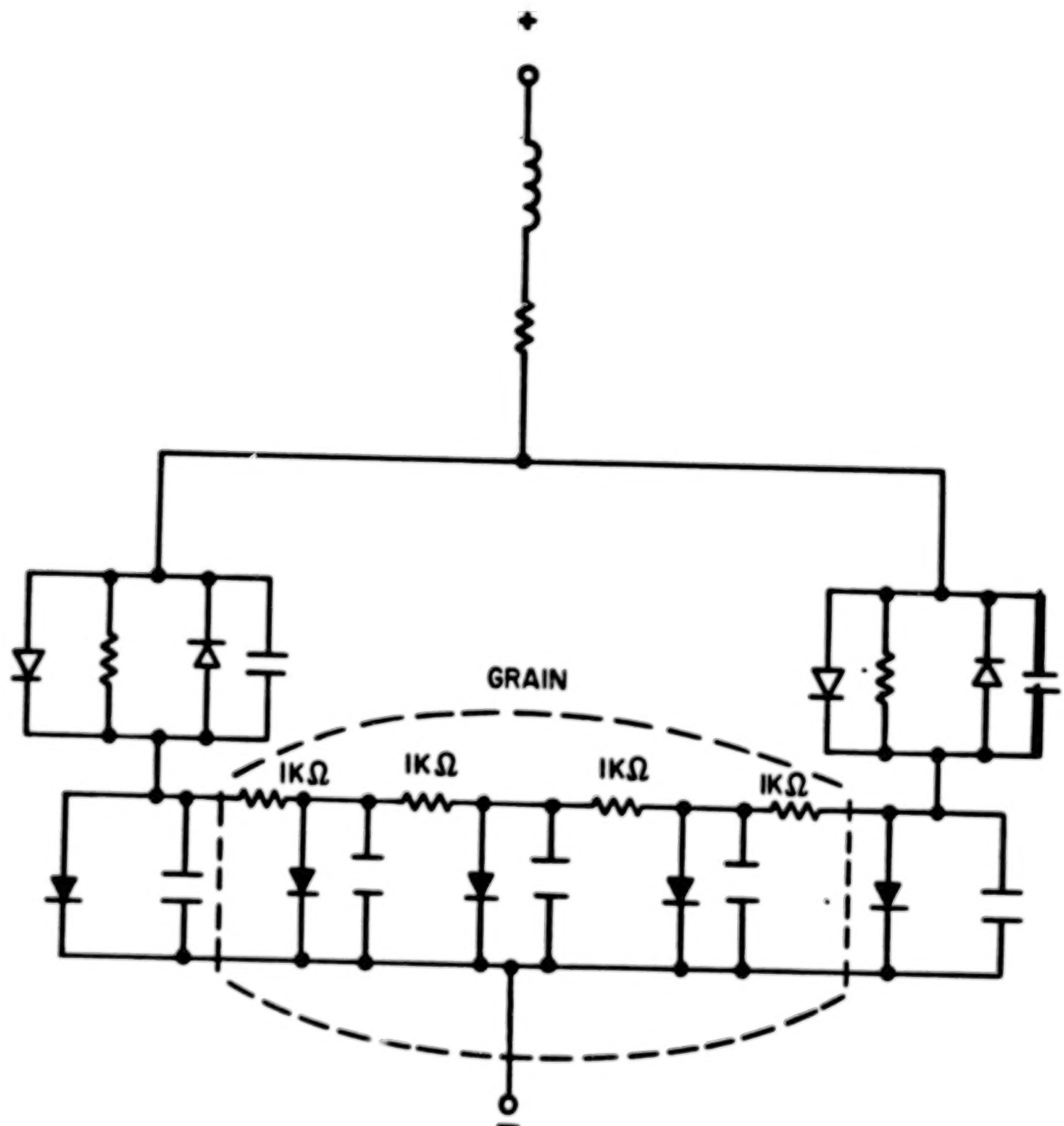
RESISTOR



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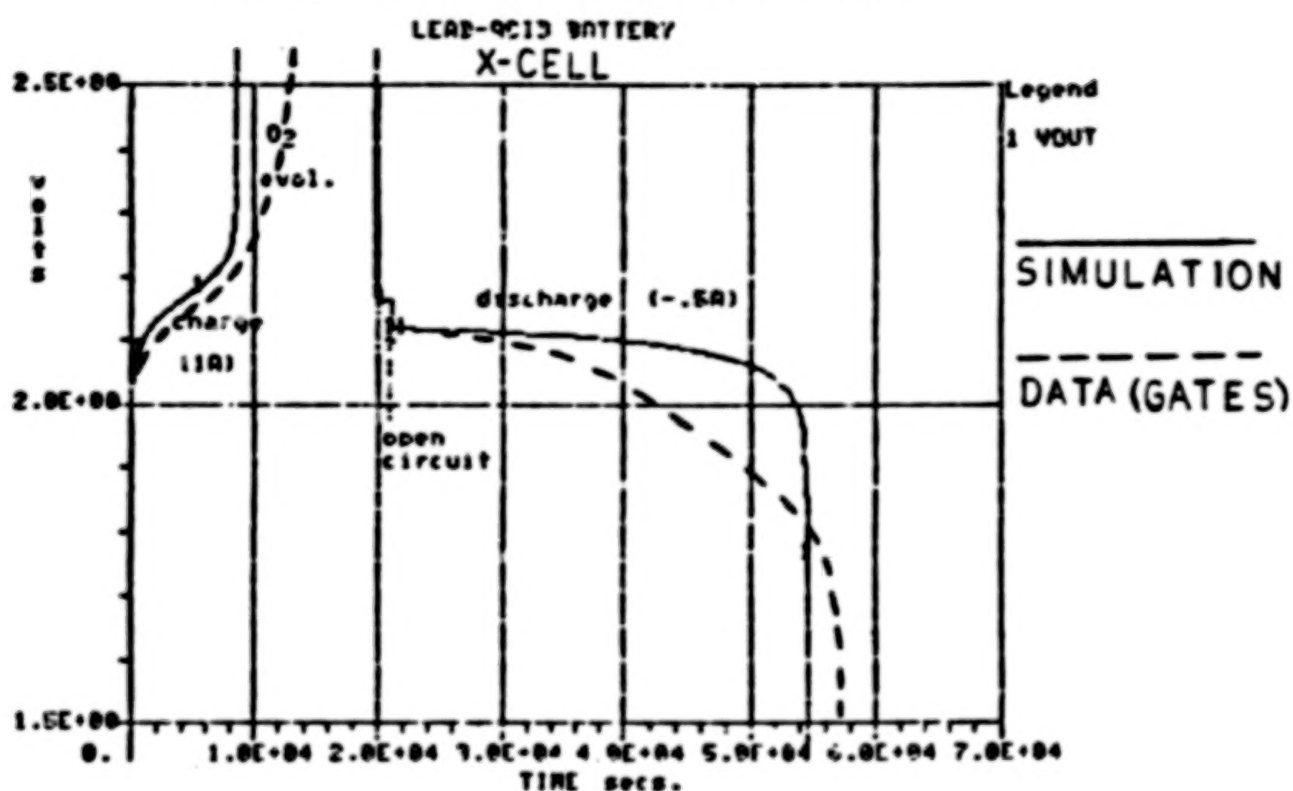


GRAIN MODEL

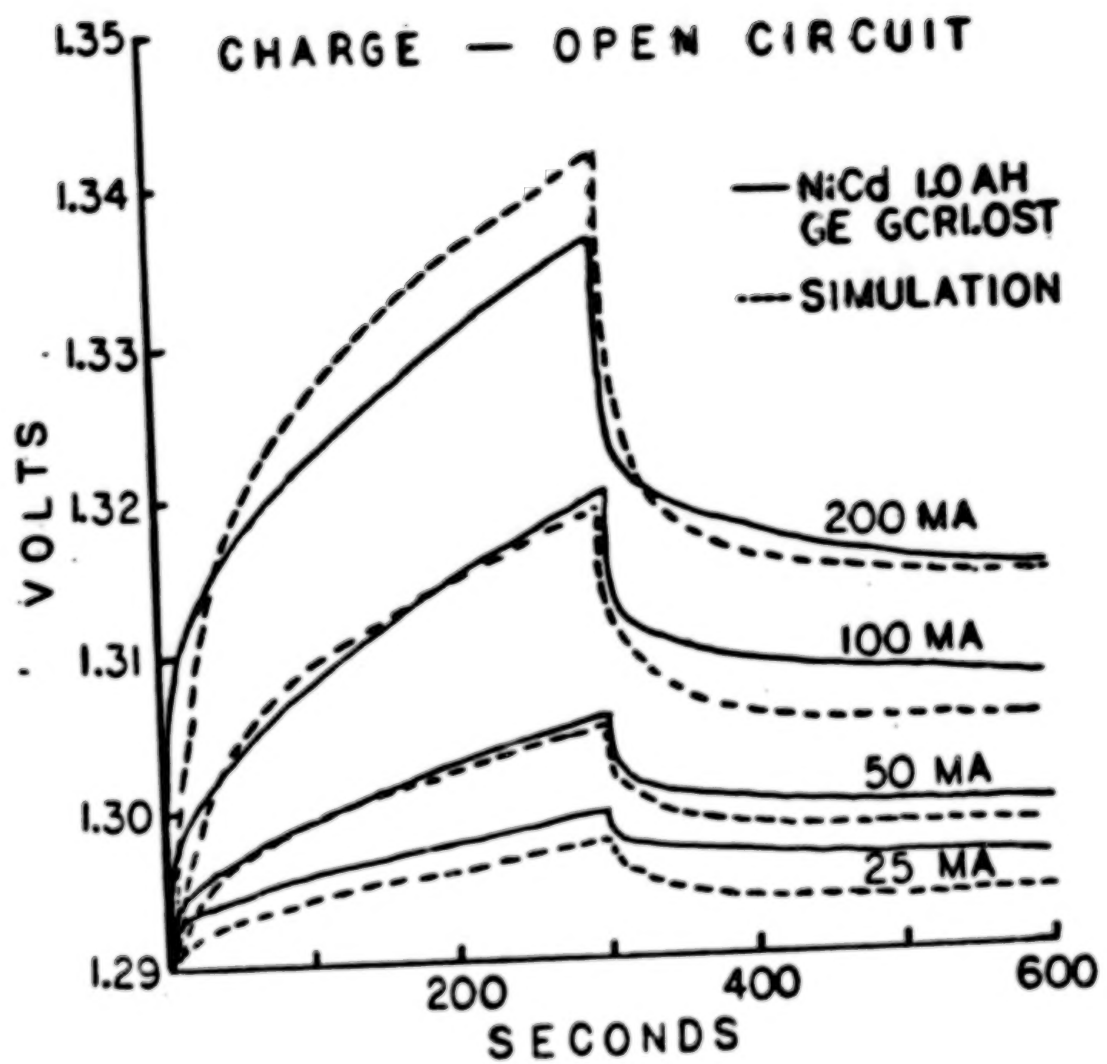


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ADVISE 23.07 DEC 07 1023 BYVLRV CR412/18 DEC 17 69:11

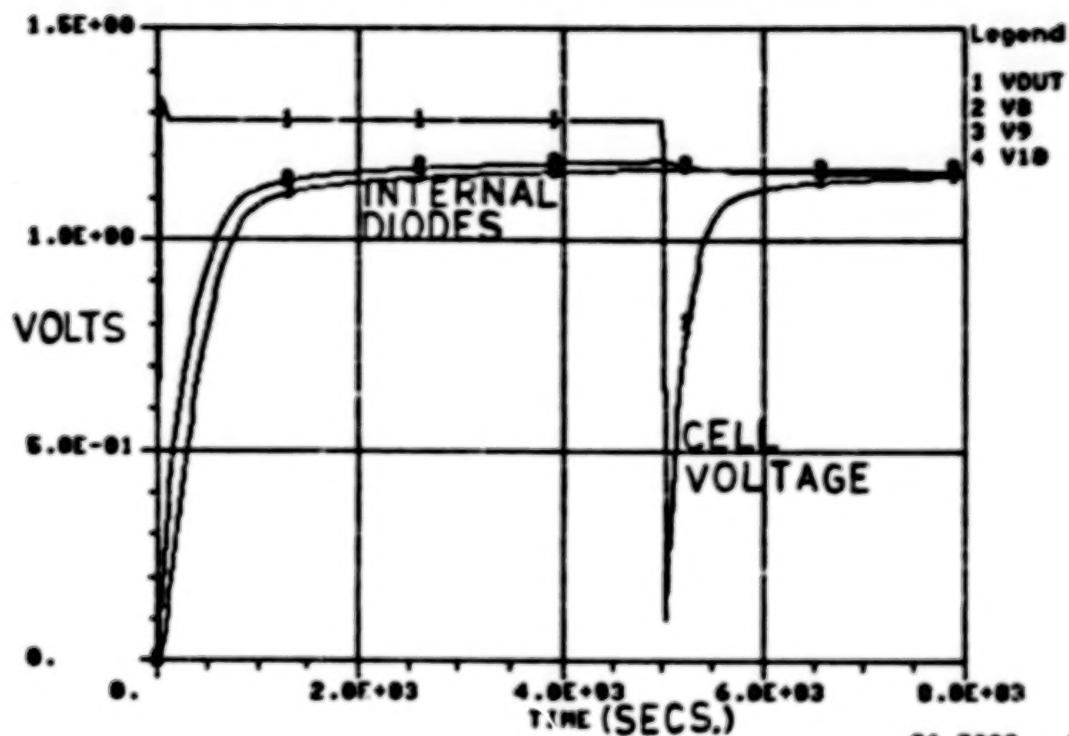


Hit return to continue: pb4 with vq's=002.137, oph's=.51



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ADVICE 1J AS OF 091892 RUN ON 09/24/82 AT 10:05:59
(25.0 DEG C) NiCd Battery Model 9/14/82



Hit return to continue: nicd6 with lin=0 0 10 1 30 1 40 0 5k 0 5010 000 - .96 8030 - .96

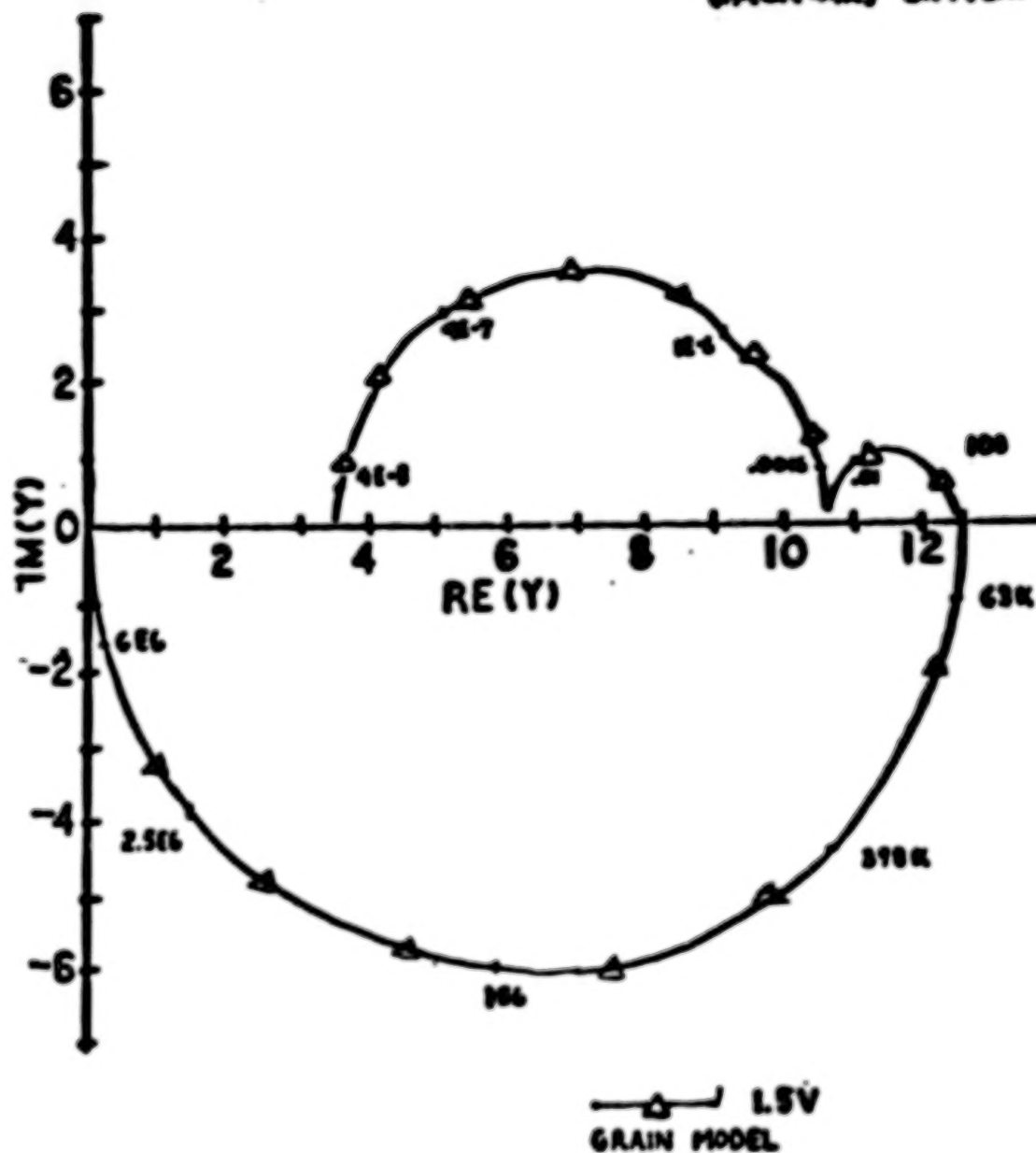
ADVISE 25 JAN 68 C 091000Z 120430Z 091227Z 02107/10107.50

N1? return to continue: nicdps uqi=0,0 .1,1.365 vin=0,0 25,2 50,0
 q1=q2=1K

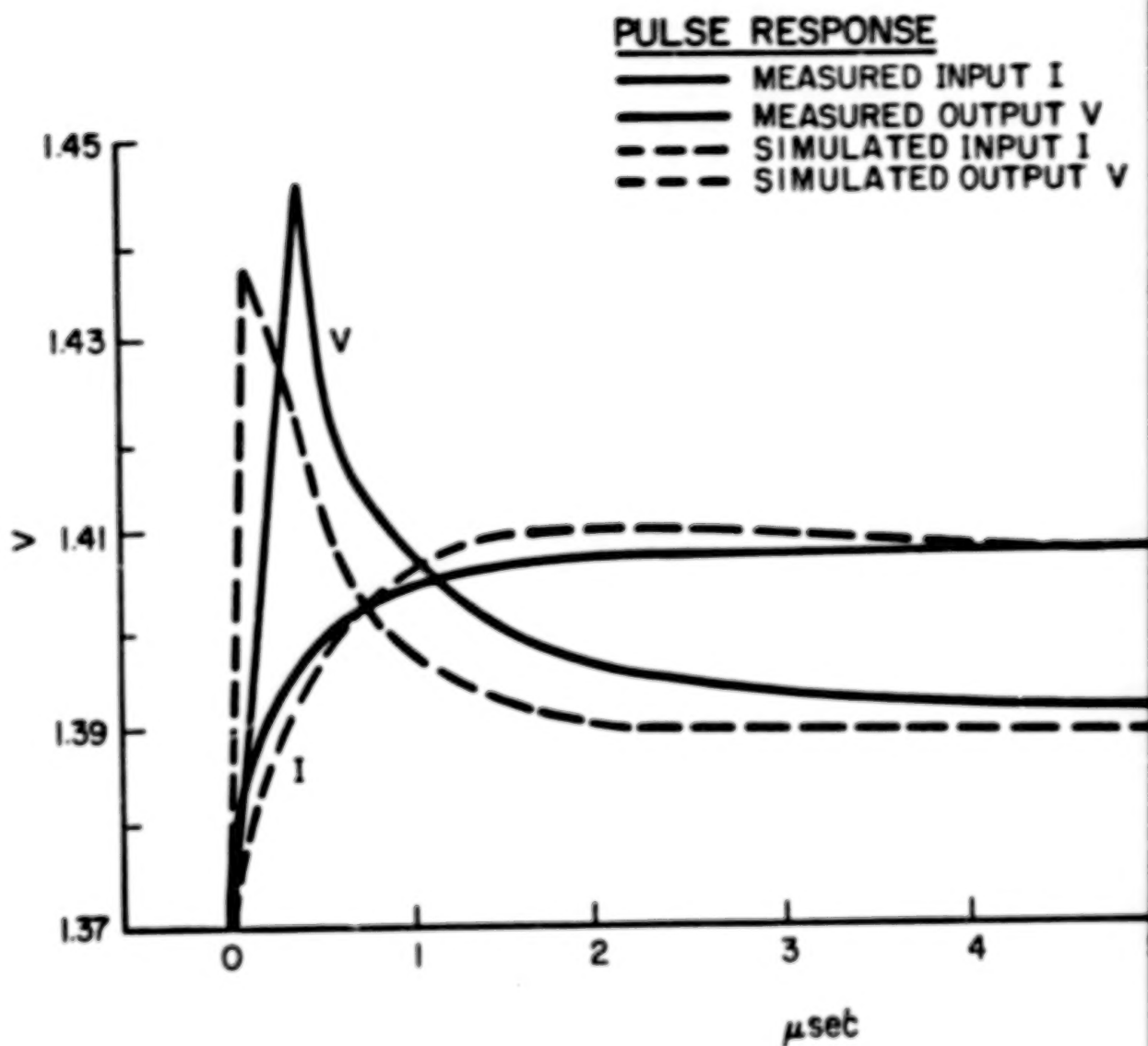
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COMPLEX ADMITTANCE PLOT

(MAGNETIC) DATA



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214

SUMMARY

1. BATTERY AS CIRCUIT ELEMENT \longrightarrow BATTERY
AS INTERCONNECTION OF ELECTRONIC PARTS

2. PIN CHARGE STORAGE DIODE+RLC COMPONENTS

- MIN. CARRIER LIFETIME $\longrightarrow \infty$
- NON-LINEAR/CHARGE TRANSPORT
- OVER-VOLTAGE DRIVE: DIODES

3. CHARGE RELOCATION/GRAINS: DIODE CHAIN

- VOLTAGE RECOVERY
- GAS EVOLUTION
- 'LOST' CAPACITY

4. SIMULATIONS: 'ADVICE'

- TOPOLOGICAL DIFF. EQU. SOLVER
- CHARGE-DISCHARGE, PULSE RESPONSE,
DEEP DISCHARGE, GASSING, VOLTAMM., AC
- WITHIN PRECISION OF MEASUREMENTS (mV)
- EASILY ADJUSTED, ANY BATTERY
- SIMULATION OF DIFFICULT EXPS
- MISSING CHARS. READILY ADDED

SESSION II

DISCUSSION

Q. Bennett, General Electric:

Most of the discussions today have been aimed at active primary systems. Many of us have applications that all for reserve systems. I'd like to know if the panel can discuss safety considerations in reserve configurations. The question is directed generally at any of the panel members.

- A. Marincic, Battery Engineering: Problems you are discussing would disappear if our reserve system can satisfy you. You can store a dry lithium battery without electrolyte as long as you can store a can of lithium that you received from a manufacturer. A storage time in thionyl chloride all alone or electrolyte is no problem so we are attacking the worse problem first. All those who are satisfied with the reserve configuration would be more concerned with mechanical solutions to the problem of activation rather than safety of the package. The safety of the package comes into the picture after the activation and most of the time it is long after it has been excluded from ever being able to hurt or anything like that. Finally, consider that an answer to the best of our ability. I don't think that is such a serious problem, compared to the problem we were attacking this morning.

- Q. Levy, Sandia National Labs: It seems to me that one of the interesting things about the lithium batteries is that adverse effects are observed after you fill the cells and for that reason I don't know that there is that much distinction between primary and reserve cells. How would you like to transport a live torpedo battery from the east coast to the west rather than transporting a barrel of electrolyte and the dry assembled battery and then go out 50 miles in the Pacific and then squeeze the electrolyte in the battery? I think there is a difference. Well, as early as 1976 we had a problem of assembling a very large battery long before anybody had any permit to transport such a material across state lines, so we transported 150-350 - five gallon stainless steel drums filled with electrolyte and that was perfectly legal. We couldn't have done the job if we didn't do it this way.

- Q. Levy, Sandia: Well, I'm pleased to hear that you can fabricate batteries safely. But, I think from the user's point of view of the incidents have occurred after batteries have been put into service I think this is a serious concern not to be just pushed aside by saying that you can safely transport the ingredients. I think that there is a legitimate problem here.

- A. Bis, NSWC: I agree, a reserve battery should be safer. We have one under test right now. The problem is with the mechanical design, for example, when the battery gets dropped sometimes there are inadvertent activations. There are activations, for example, we have to face situations like fire aboard ships and aircraft. What happens to your reserve battery under those conditions? I should have brought a video tape. We have a fire ball which would fill essentially half this room of a reserve battery in deflagration test. The battery was not activated, it activated when we exceeded the burst of pressure of the disc but by far, and those things can happen. To say categorically that a reserve battery is inherently safer, I can't buy that.
- Q. Marincic, Battery Engineering: Nobody said it was safe. But it is safer than a primary battery. Otherwise we would be discussing not to transport lithium from a sealed container. Part of the problem of reserve battery is that. Accidental activation is that. Accidental activation is that mechanical problem that I mentioned earlier. Of course, fire danger always exists there whether you are transporting one or many. Safe, no I never said that.

COMMENT

Marcoux, Hughes: I just thought I'd attack Chuck's question since I can't answer it and the vulnerability of the question lies in the fact that too often the systems are chosen as alternatives to reserve systems and when you go to reserve system packaging you know as well as I, you start to lose incredible energy density advantages and in fact why the hell bother with it at this time because you still buy a lot of silver. Zinc's remotely activated and I know you're looking for an alternative. That's what you're talking about. There might be a contradiction in terms here Chuck; it may not be an appropriate application.

COMMENT

Bis, NSWC: Well, I have one last comment on reserves. Many of your reserve batteries have a common electrolyte feeding. All the cells, be it series parallel or whatever have seen very severe problems. I don't think they are unsurmountable but we have one in the Navy with a long wet stand and this unit is recovered and we've had massive explosions because of dendritic growth backs up through the fill tubes. It's a real problem. I mean the problem is under investigation and I think it can be solved. But I don't think it sits in a reserve mode. There are applications whereby there are personnel around the battery after it's been activated and you do pay a severe weight and volume penalty when going into reserve.

- Q. Seiger, Seiger Associates: Several years ago there was an emergency transmitter located aboard some aircraft that was removed and there were some stories going around that it was associated with the batteries. Could Dr. Marincic relate to us some of the details about that? I assume he's knowledgeable?
- A. Marincic, Battery Engineering: I have to tell you I don't know anything about batteries that blew up on an aircraft.
- Q. Seiger, Seiger Associates: Does anybody else know about it? Somebody must.
- Unidentified Speaker: Are you referring to the first attempt to put SO2 batteries on the aircraft? Believe it or not I have never heard of it. I have seen opening of ground panels on rectangular cells, but that's a different story; not on the aircraft.
- Q. Seiger, Seiger Associates: Does anybody know about it?
- A. Lackner, DRED: Yes, earlier in Canada there was a call for complete removal of all lithium batteries in ELT. There were several accidents involving venting. One plane had to come in on emergency procedures and FAA put out a TSO (Technical Service Order) and I don't remember the date on that but all lithium batteries were removed from Civil aircraft both from ELTs and flight recorders. They subsequently went out on the market and carried out a test plan and there was one manufacturer that met all requirements of test plan and as far as I know lithium batteries are back and ELTs, and flight recorders on all aircraft.
- Q. Watson, Saft: Frank, you showed us graphic pictures this morning of some high rate thionyl-chloride cells that detonated when they were exposed to some of your abusive tests. You also mentioned they had a vent mechanism in them. Did you do any analysis or did you work with the manufacturer of those cells to determine when the vents would not prevent that cell from exploding?
- A. Bis, NSWG: Well, first of all I don't care what kind of vent you put in, the vent you saw was a true detonation. We have other cells where actually the vents did open up and materials were coming out and subsequently they detonated after venting. So, we talk about vents and the pressure rises. We're seeing this in some of these we're not measuring but they are rapid enough that there is no vent mechanisms that's going to handle it; it will override any vent. We're talking about complete schrapnelization of the can. For example, when there is nothing left of the can, when you can't even find a tear in it. Also

we have a program in the charging of SO₂ cells and we're seeing pressure rise time in the order of 40 milliseconds. So these things are rising faster than the SO₂ system under charge now; faster than we can get propellants to ignite. So, I don't care what type of vent you put in if you get to the situation, the vent will not handle it.

- Q. Marincic, Battery Engineering: Before I forget my question, we heard this morning the definition, or at least experience, with so called lithium limited batteries and cathode limited batteries in the case of thionyl-chloride. I'd like to present to this audience a simple picture of the way I see it. There is no such a thing as a truly cathode limited battery in thionyl-chloride system. When you say cathode you have to talk about carbon or electrolyte. I can make a lithium limited battery with a thionyl-chloride electrolyte and in order to convert it to carbon limited without ever opening it, all I have to do is to raise the rate of discharge.

So are we talking about electrolyte limited. If you are talking about carbon limited how do you calculate the capacity of the carbon electrolyte? Did the manufacturer tell you? And the only way I know to make electrolyte limited is to discharge it at a very, very, low rate. Do we have a clear distinction in the safety behavior of the two types?

- A. Abraham, E.I.C. Labs: The thionyl-chloride cell you were talking about which I could have made myself if they were not made by the manufacturers, and they were carbon limited cells.
- Q. Marincic, Battery Engineering: They were carbon? Why do you say they were carbon limited? How do you know that? How do you calculate the capacity that you expected of your carbon?
- A. Abraham, E.I.C. Labs: Well, it's just based on theoretical values other people have seen. What I mean is something on the order of 200 hours per cc.
- Q. Marincic, Battery Engineering: Personally, I have gotten four ampere hours per cc of carbon on these particular conditions. So, if I had that cell it would be carbon limited.

- A. Abraham, E.I.C. Labs: The experiment we have is lithium thionyl-chloride cells with a reference electrode inside and we follow the potential of each of the electrodes. OK? So, we know exactly which electrode is polarizing and we know that it is a positive electrode which is polarizing.
- Q. Marincic, Battery Engineering: That's very important to know that when you say that, because if it is current dependent...
- A. Abraham, E.I.C. Labs: That was the second point in my summary, i.e. lithium limited cells, where you can remove all the lithium at the end discharge, I think is safe.
- Q. Marincic, Battery Engineering: But you didn't have a reference electrode in there either, that is very important.
- A. Abraham, E.I.C. Labs: There were three reference electrodes you were talking about because all that work involved measurement of each electrode. In fact, that is what we are doing at the moment with copper/dioxide cells. I'll show you some discharge curves there but I can't really say which electrode is where. So what we're doing at the moment is to make cells with three electrode systems so we can measure each of them.
- Q. Marincic, Battery Engineering: Now I had another question. Did you have analysis of your electrolyte before you started your test? Specifically, what was content of hydrolysis product in the electrolyte?
- A. Abraham, E.I.C. Labs: We do all our work in a dry box and the electrolyte, for example, is dissolved. It is prepared in the best solution we can make for it.
- We make lithium-chloride and aluminum-chloride and melt it, pre-electrolyte the melt and then the thionyl-chloride is dissolved very carefully in lithium.
- Q. Marincic, Battery Engineering: But did you do your analysis?
- A. Abraham, Battery Engineering: We did not measure it but I think it should be very small. It's done under very... In fact, I have an infrared spectrum and I don't see any water leaks at all.
- Q. Marincic, Battery Engineering: On the infrared? On the finished electrolyte?
- A. Abraham, E.I.C. Labs: Right, right. It's very important, I think it's a very dry condition.

- A. Marincic, Battery Engineering: Also what I happen to think has a lot to do with behavior of your cells on overdischarge. Very important.
- Q. Schlaikser, Duracell: I wanted to ask the gentleman from Electro-Chem Industries whether his cells were shock sensitive and also were they lithium limited or carbon limited or electrolyte limited?
- A. Krehl, Wilson Greatbatch, Ltd: Carbon limited cells. In fact, our capacity or utilization of carbon is about three ampere hours per gram for a D cell. It might be slightly less than that, it might be 2.8. That's a fairly typical value.

It would be a nominal rate of about 250-400 ma. If you go to a higher rate than that, we drop off the capacity quite a bit. One amp. rate would get about eight or nine amp hours; so amp hours per gram drops off roughly one-half. Saying we are in lithium excess would be a better way of putting it.

Shock sensitivity: We have not seen that as far as any of the tests we have performed. We did overdischarge extensively for many cells at high rates, (D cells at 5 amps), and again this would be where you take a cell and force overdischarge it without the open circuit break but force into a voltage reversal. We've done that for about 100 hours on particular cells and we actually shot the cells, using a 410 gauge shotgun. That might be a very calibrated test but nobody else would swing a hammer at the cells. That's how we did it and we haven't seen any shock sensitivity in the cells to date.

- Q. Zimmerman, Aerospace Corporation: I noticed in the last two presentations what seemed to be a correlation between these voltage fluctuations and a tendency to vent. Is this correlation real, and would you give any indication what the possible origin of these fluctuations and the voltage might be?
- A. Abraham, E.I.C. Labs: Well, what we are doing at the moment is to study, to really categorize, what is happening with lithium SO₂ cells. For example, we're seeing when you overdischarge in many cases you see voltage of fluctuations, and we don't really know exactly which electrode is doing this, as in the case of the SO₂ cells.

We knew, for example, in the case of thionyl-chloride where we had reference electrodes in those cells, the fluctuations were mostly at the anodes. We believe in those cases this is caused by the making and breaking of contacts of the lithium with the the thionyl current electrodes. I don't think that is the primary thing. I

think that part of the fluctuation is due to a resistance build-up in the cell. You have decreased the amount of SO₂ and you've produced reactions for lithium and acetonitrite at a mode that causes some of the fluctuations too. So, we hope to talk about it and deal with it later.

A. Taylor, Duracell: I suppose that one of the ways I can speak is by answering the last question. Sometimes I wonder if people read the literature. Sometimes I wonder frankly, if the people who do the testing read what the manufacturer recommends to do beforehand. I think that is the reason why you get these voltage fluctuations under conditions by the way in which the manufacturer states that you shouldn't use the cell and is aware of the hazard that might be involved. Anyway, I think that reactions that go on are lithium and nitrite-lithium deposited on the cathode that react with sodium-nitrite. This must have been published back in 1977. Whose money are we spending to look at this? Resulting gas methane and methane causes fluctuations in the voltage. This is quite a simple explanation. The hazard of cells, lithium SO₂ cells, which are tested in conditions not recommended by the manufacturer, are simply a reaction to lithium and under acetonitrite conditions of reversal.

The reason why you get that sort of reaction taking place at low temperatures cases is, if one takes a cell into voltage reversal at low temperatures then I think that the simple scenario is that you again get lithium and acetonitrite. They are present in the cell with the tendency to react. Chemical reactions, I think as we all know, are slowed down by temperature so it's quite logical to assume that during that quiescent state under discharges you're generating hazardous chemical and you merely have to warm the cell back up to room temperature where you then will get these two reactions at quite substantially increasing rates. So scenarios for low temperature are no more different than the scenarios for room temperature for a reversal condition.

What I am trying to say is, among other things, I think that the chemistry is understood and that one can predict what is going on with voltage reversal in lithium SO₂ cells. Until we change the chemistry to nitrite, for example, one can face the fact that there are limitations to its use. The scenario that we saw presented, I think to EIC, to type A and type B cells in a way were going over old history. The type A and B, I presume were balanced and unbalanced cells. Lets not continue to talk about this year after year. We now have found cell versions which are meant to extend the safety of the lithium SO₂ cells under voltage reversal conditions at given discharge rates. Again, conditions under which problems can happen are known and I for one would not like to continue to come to meetings and hear about this again and again as if this were something new. The comment was made at the start of this meeting that we should try and be posi-

tive in thinking about lithium systems and testing of them. I wish people would start to do that and follow that sort of thought process rather than kill the darn things. More points if I may; I was quite happy to hear the fellow from Electro-Chem Industries talk about voltage reversal test.

I don't know how we all do it in general but I was pleased to hear him say he didn't limit his power supply. If we don't do that in the Navy, Marines, Air Force, and whatever I think that maybe we should consider Electro-Chem industry type testing as a more relevant one. I can take a 50 volt power supply and sure force an SO₂, or any other battery in reversal and kill the hell out of it but it may not happen under real conditions and that's what you really want to find out.

SESSION III

"WHICH METHOD OF CHARGE CONTROL PROVIDES THE MOST
RELIABLE OPERATION FOR NEAR EARTH OR SYNCHRONOUS MISSIONS?"

Sidney Gross
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PROSPECTS AND PROBLEMS OF SPACECRAFT BATTERY CHARGE CONTROL

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This paper serves to introduce the subject of battery charge control by identifying some of the future possibilities and some of the present problems. In so doing, a view is taken of charge control that is broader than generally used. There are many issues that can involve the charge control system. In fact, this paper does not emphasize the question, "What is the best charge control method?" Instead, questions are posed which will help find the best method.

The most important concern with charge control is the effect of different procedures on battery performance and battery life. Performance and life are distinguished, for they are not necessarily the same. Thus, a charge method that results in high discharge voltage and high capacity may not necessarily be promoting long life. The immediate relationship of charge method to performance is relatively easily obtained, though surprisingly the scope of parameters investigated is often relatively narrow. The relationship of charge method to life is the biggest concern, and the most difficult to establish.

An interesting speculation is whether a cell is degraded or fails mostly because it had N discharges or because it had N charges. Which caused the greater stress? Can this partitioning be done, and if so, how? About 61 percent of the battery lifetime in LEO is spent in the charge regime; over 99 percent of the time in GEO is spent in charging. Charging could easily exert a major influence. Assuming we understood the failure mechanisms and their relationship to charging parameters, we would be able to devise charge methods most favorable to long life.

What might be some of the candidate features of a charge control method that gives the longest life? To illustrate the many factors available, the following list is offered:

- o Cell behavior during charge is used to characterize and screen cells;
- o Charge current is varied in a specific manner;
- o a.c. current is superimposed on the d.c. current;
- o Pulse discharges are periodically imposed during charge;
- o Cell temperature is programmed through a specific cycle during charge;
- o Rest periods are imposed during charge;
- o Cells are not always brought to a full charge, and the maximum state of charge at the end of charge is varied from cycle to cycle;

- o Periodic brief tests are imposed during charge, and cell state-of-health is determined by computer diagnosis;
- o Based on the determined cell state-of-health, the charge control law is modified with time;
- o Periodic brief tests are imposed during charge, and cell state-of-charge is determined by computer analysis;
- o Periodic reconditioning is performed by use of a special charge scenario.

Before endeavoring to work out the basic relationships between cell life and charge parameters, the immediate problems must be faced of applying existing charge methods to spacecraft applications. For any of over a dozen charge methods (e.g., Ref. 1), there are a myriad of questions that arise about the method, its proper implementation, its applicability to various orbits, the performance that may be expected, and its strengths and weaknesses. Some of the questions that arise are as follows:

- o Should multiple batteries be charged sequentially or all at the same time? If multiple batteries are charged at the same time, should they be paralleled or are dedicated chargers necessary?
- o What is the sensitivity of charging behavior to the number of batteries charged? Should the decision of the best charge method be related to the number of batteries in the system?
- o Where voltage-temperature compensation is used, how many curves are appropriate?
- o Where trickle charge is used, how many selectable rates are needed?
- o If charge voltage is limited, has high rate charging proven to be a problem? How high a rate is safe?
- o How is it determined if the battery is really charged?
- o How best should a shorted cell be accommodated? Is an automatic charger adjustment worthwhile?
- o How important is a big data base of flight experience in obtaining good performance with any particular method?
- o What are the clever twists that have been found to be either important or undesirable with each method?
- o What are the problem areas with each charge method?
- o Should the pressure in Ni-H₂ cells be used for charge control, or merely monitored?
- o How do we know when we have a good charge method?

- o How does the charge method perform in off-design conditions or following the possible failures?
- o How efficiently is the solar array used by the particular charge method?

Hopefully answers will be forthcoming from these questions, which are posed in the spirit of Kipling:

I keep six honest serving-men
(They taught me all I knew):
Their names are What and Why and When
And How and Where and Who.

Kipling: The Serving Men

References:

1. S. Gross, "Rapid Charging of Lead-Acid Batteries", Proceedings of IEEE Industry Applications Society, Oct. 1973.

A COMPARISON OF CHARGE CONTROL
RESULTS FOR SUN ORIENTED VERSUS FIXED ARRAY MISSIONS

GERALD HALPERT
SPACE POWER APPLICATIONS BRANCH
GSFC

NOVEMBER 17, 1982

A COMPARISON OF VOLTAGE LIMIT CHARGE CONTROL
FOR FIXED ARRAY AND SUN ORIENTED ARRAY MISSIONS

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INTRODUCTION

The voltage limit/current taper (V_T) method of charge control of Nickel Cadmium batteries has been utilized successfully on many Low Earth Orbit (LEO) GSFC missions. For the most part, these spacecraft have contained sun oriented arrays (two or three axis stabilized) to provide the maximum current at the beginning of the sunlight period. The latest use of this technique has been on Solar Maximum Mission (SMM), launched in February 1980 and Landsat D launched in July 1982. Both of these spacecraft utilized the Multimission Modular Spacecraft (MMS) consisting of the Modular Power Subsystem (MPS). The MPS utilizes a peak power tracker which provides maximum power and therefore, current when the spacecraft emerges from the Earth's shadow. The maximum power is available throughout the daylight period. Thus, the batteries are charged quickly to a preset temperature compensated voltage (V_T) limit and allowed to current taper until the end of the daylight period (thus, controlling the amount of overcharge). A typical orbital profile is given in Figure 1.

The Earth Radiation Budget Satellite (ERBS) is projected to be in a 610-kilometer circular orbit with an inclination of 46 to 57 degrees with respect to the Equator. Its solar array is fixed with respect to the spacecraft. The resulting orbital power profile differs considerably from the Solar Maximum Mission (SMM) or Landsat-D spacecraft operating in a Low Earth Orbit with a sun-pointing solar array.

The ERBS profile is such that when the spacecraft emerges from shadow, the solar array angle to the Sun is minimal. Thus, the current available for charging the batteries is minimal. As the spacecraft continues in orbit, the solar array points more directly at the Sun, which increases the available charge current to a maximum at midday. The charge current then decreases as the solar array points away from the Sun through the remainder of the daylight period. Further, with a fixed solar array, the spacecraft (in different orbital planes around the Earth) assumes different angles (Beta angles) between the normal to orbital plan and the sunline. The power profile indicating the current available, for each of the two batteries, under three different Beta angle conditions in the ERBS orbit (90, 65, and 10°) is given in Figure 2. There has been only limited cell and battery testing in this type of orbital profile to date.

This paper will provide a comparison of V_T Charge Control operation of SMM, Landsat-D and ERBS profiles.

Charge Control Considerations

Regardless of orbital profile, there are some basic cell performance and operational characteristics that must be considered in order to plan a long lived reliable power system. These are given in Table I. On any given orbit, the charge control voltage and profile will have a profound affect on battery performance as judged by discharge voltage and capacity. In addition, the charge to discharge (C/D) ratio will affect the degradation and temperature of the batteries. There are also subtle affects such as charge voltage, cell efficiency, overcharge etc. which appear to have little effect from orbit to orbit but have a profound effect on the long term operation of a battery.

The basics of V_T type charge control are summarized in Table II. It must be understood that the electrochemical cell is a voltage device, that is, it requires an adequately high potential (charge voltage) to bring the battery to a full state of charge. It operates efficiently, as described in Table II, when the voltage level

(VT) is reached at 65 percent of the ampere hours removed on the previous discharge. The remaining 35 percent is returned in the current taper mode. In addition, some overcharge is required. The extent of overcharge is controlled by the charge/discharge ratio. It governs whether the battery reaches the full state of charge or is subjected to overcharge and heating. The recommended operational charge/discharge ratios as a function of temperature for 25 percent depth of discharge is given in Figure 3.

The available eight operating temperature compensated V_T levels in the MPS are given in Figure (4). For 15-25 percent depth of discharge, V_T level five has been found to be the most optimum. The other levels can be utilized in cases where there is extreme cell degradation (higher V_T level) or a cell short in one of the parallel connected batteries (lower V_T level). The flexibility of the system is illustrated in Figure 5, where the profile for V_T 4 and V_T 6 charge control are compared. Note that there is only a small increase in the time to reach V_T 6 over V_T 4 resulting in only slightly more overcharge. This type of operation is considered quite forgiving in that even though the two levels are 40 MV/cell apart, there are only slight differences in the performance. Adjustments for long term effects can be made at a later date.

Operating in this manner has been shown to be quite reliable and provides long life. Data from SMM orbit 14,858 (Figure 6) provides an indication of the three batteries operating in parallel and a measure of their current sharing—a strong indication of successful operation. In the Figure, it is impossible to see anything but minute differences in current. The buss voltage after almost three years is still 1.220/cell average at 5°C.

The block diagram of the MPS is given in Figure 6 and indicates that the three 22 cell 20 AH/or 50 AH batteries are in parallel on the buss for both charge and discharge.

Life projections from the results of testing in this manner have been summarized from the NWSC/Crane test program in Figure 7, five years of operation are predicted. At 20°C and 25 percent depth of discharge in Low Earth Orbit using the present generation Nickel Cadmium Cell with Pellon 2505 MI Separator. This data also includes the NASA Standard 20 AH and 50 AH cells manufactured by General

Electric (P/N 42B024AB06/07 and 42B050AB20/21) manufactured to the NASA Standard 232A2222-84 Manufacturing Control Document (MCD). The NASA Standard batteries are designated by their manufacturer McDonnell-Douglas as 70A237003 and 70A237005 for the 22 cell 20 AH and 50 AH batteries respectively.

The ERBS-Fixed Solar Array Test

As indicated above, there is little information on the performance of Nickel Cadmium batteries charged in the voltage limit/current taper in the ORBS orbital profile (see Figure 2). To determine the suitability of this method under these conditions, a parametric test on 50 AH cells conducted at the NWSC/Crane facility was performed to evaluate the relationships between voltage level temperature and beta angle. The program outline is given in Table III and included 24 hours of operation following an activation cycle of $C/2$ charge to $V_T 6$ followed by current taper to $C/15$. The ERBS profile was provided by a microprocessor which utilized 250 steps to simulate the expected current.

Typical results for specific orbits for NWSC pack 50E are given in Figure 8 (Beta 90°), Figure 9 (Beta 65°), and Figure 10 (Beta 10°). In the Beta 90° and Beta 65° , the current (solid line) increases during the day period in the expected profile until the prescribed V_T level is reached. The current tapers until it reaches the same value of current available from the array, then drops in following the profile. In the Beta 10° case, the spacecraft was assumed to be in continuous sunlight and thus, the batteries were in continuous taper throughout the 24 hour period.

The effect on charge/discharge ratio for the five cell pack (50E) subjected to the parametric test is given in Figure 11 for Beta 90° and Beta 65° for the two battery case and in Figure 12 for the one battery case. The recommended charge/discharge ratios from Figure 3 are shown for comparison. It was determined that the $V_T 5$ level used for SMM and Landsat D would not adequately charge the batteries in the Beta 90° or 65° ERBS profile. V_T level 6 also was not adequate for B 90 case, but was higher than desired for the beta 65° case as was $V_T 7$ for the beta 90° case.

The data for the Beta 10 case is given in Figure 13. The end of charge current and total ampere hours in at the V_T 3, 4, and 5 levels are provided. At V_T 4 for example, at 15°C the 22 cell battery voltage would be 30.9V at a current 2.1 amps. This would provide a continuous heating of 65 watts for each of the three batteries and would necessitate a continuous requirement to remove 195 watts from the MPS.

The Augmented Charge Control System For ERBS

It was determined that a further enhancement of the charge control system was necessary to avoid significant overcharge and heating. The method selected required an ampere hour integrator to throttle the current to 0.75A trickle charge (one of three constant current levels available in the MPS) when the desired C/D was reached. The prime contractor for ERBS, Ball Bros., provided a series of C/D ratio vs. temperature curves from which to choose the desired C/D ratio. These are given in Figure 14 together with the GSFC recommended range. For the follow-up test to evaluate the effect of the ampere hour integrator, augmented charge control system curve two was selected.

The results of the follow up test with integrator are given in Figure 15-18. The profiles for testing were further delineated to simulate the expected updated ERBS operation. These were provided by H. Culver at GSFC and Ball Bros. Two sets for tests were performed for Beginning Of Life (BOL) and End Of Life (EOL). They also included extending test conditions to the Beta angles to 90° , 65° , 45° , and 15°C . All tests included charging to V_T 6 only.

In the Beta 95° BOL test (Figure 15) operation was at V_T 6 the C/D ratio did not reach the preset value, and therefore, there was not trickle charge. At Beta 65° (Figure 16), there was a few minutes of trickle charge at the 0.75 cmp rate. It increased at Beta 45 and was significantly long at Beta 15° .

The quantitative summary results for the follow up tests are given in Table IV. The final six columns tell the story. The TTVL column is the time to V_T level, the time to taper charge. The following column is the time in trickle charge (note

that at B90 there was no trickle charge). The final three columns are the charge to discharge ratio up to the trickle charge, with the trickle charge and finally, the last column is the estimated value if there had been no provision for trickle charge.

For the Beta 90 case, a C/D of 1.014 is not adequate to maintain the batteries in the full state of charge. $V_T 7$ will have to be used at this Beta angle and depth of discharge. The remaining conditions indicate that the desired C/D was reached utilizing the integrator augmented charge control schemes. As can be seen in the final column, significant overcharge was avoided.

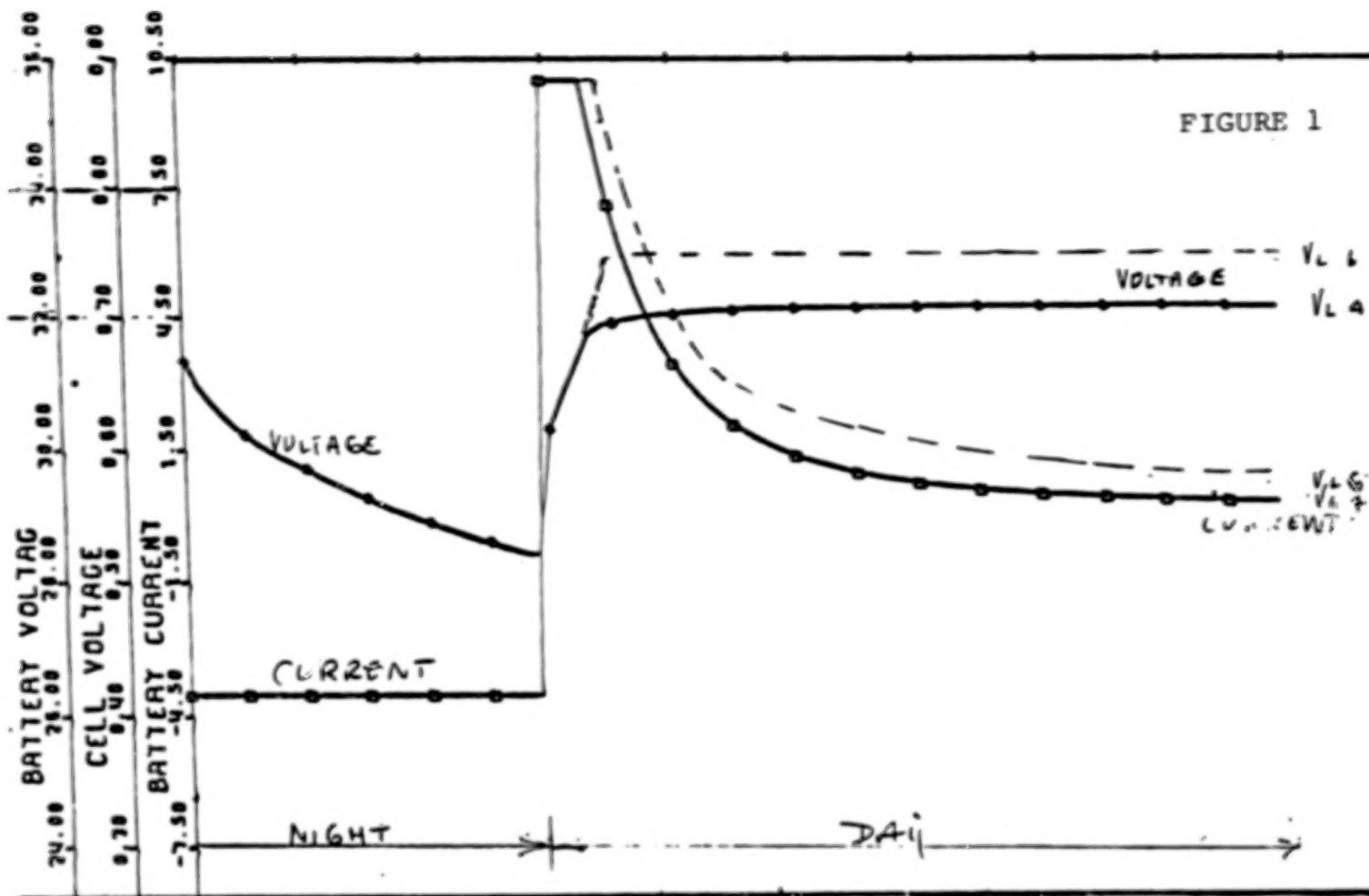
Summary And Conclusions

The voltage limit/current taper charge control method has been successful in providing long lived spacecraft utilizing batteries in parallel on the charge and discharge buss as evidenced by SMM and Landsat D.

However for the ERBS profile, use of the V_T limit, alone, as a charge control device resulted in C/D ratios which were, generally, well above or below the acceptable operating values. Operating at the higher V_T level, and reducing the charge current to 0.75 A when the acceptable C/D limit was reached minimized the battery overcharge. A microprocessor was used to control the test and served as an ampere hour integrator providing the signal to switch to the trickle-charge mode.

The advantage of this technique for charge control is that overcharge and heat dissipation are minimized. In addition, the battery is charged at V_T levels that were found to be successful in the past.

TYPICAL VOLTAGE LIMIT/CURRENT TAPER CHARGE CHARACTERISTICS



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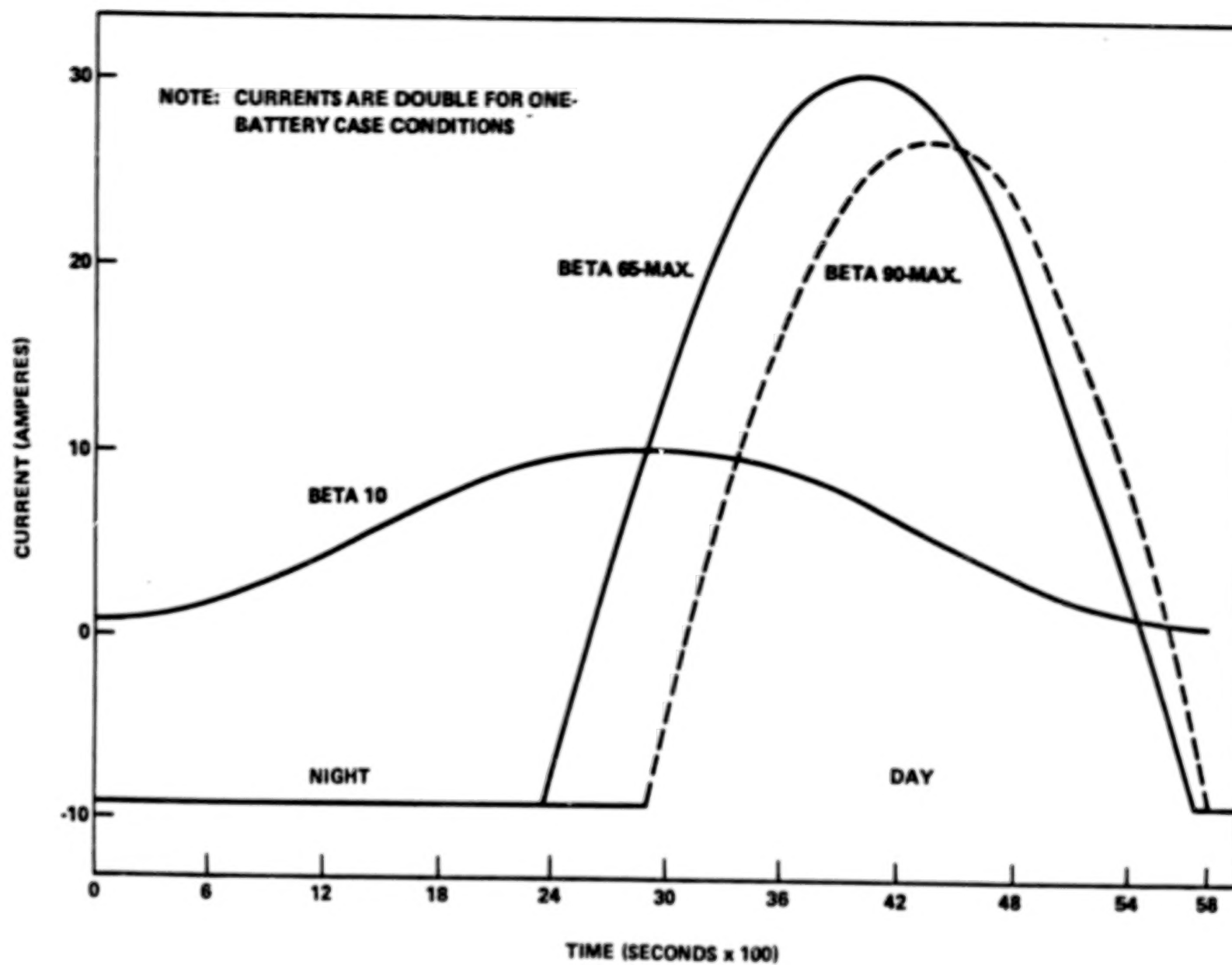


Figure 2. Current Profiles for ERBS Fixed Solar Array

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CONTROL CHARGE CONSIDERATIONS

- o CHARGE VOLTAGE AS FUNCTION OF
 - RATE PROFILE
 - TIME
 - TEMPERATURE
 - DEPTH OF DISCHARGE
- o CHARGE/DISCHARGE RATIO
 - EXTENT OF OVERCHARGE
 - HEAT REMOVAL CAPABILITY
- o CHARGE CHARACTERISTICS WITH LIFE
 - VOLTAGE
 - CHARGE ACCEPTANCE
 - EFFICEINCY
 - UTILIZATION
 - PRESSURE
 - SECOND PLATEAU

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239

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THE BASICS OF CHARGE CONTROL

- o CELL/BATTERY - A VOLTAGE DEVICE
- o OPERATIONS EFFICIENTLY - VOLTAGE LIMIT (VL) CONTROL METHOD
 - MODERATE-HIGH CURRENT TO VOLTAGE LIMIT (V_L) (65%)
 - REDUCED CURRENT AT VOLTAGE LIMIT (35%)
- o VOLTAGE LIMIT IS TEMPERATURE COMPENSATED
- o AMP HRS CHARGE/AMP HRS DISCHARGE RATIO ALSO USED FOR CONTROL
 - PROVIDES MEASURE OF OVERCHARGE (HEATING)
- o BATTERIES IN PARALLEL ON BUS
 - EQUAL CURRENT SHARING IS IMPORTANT FOR PROLONGED OPERATION

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241

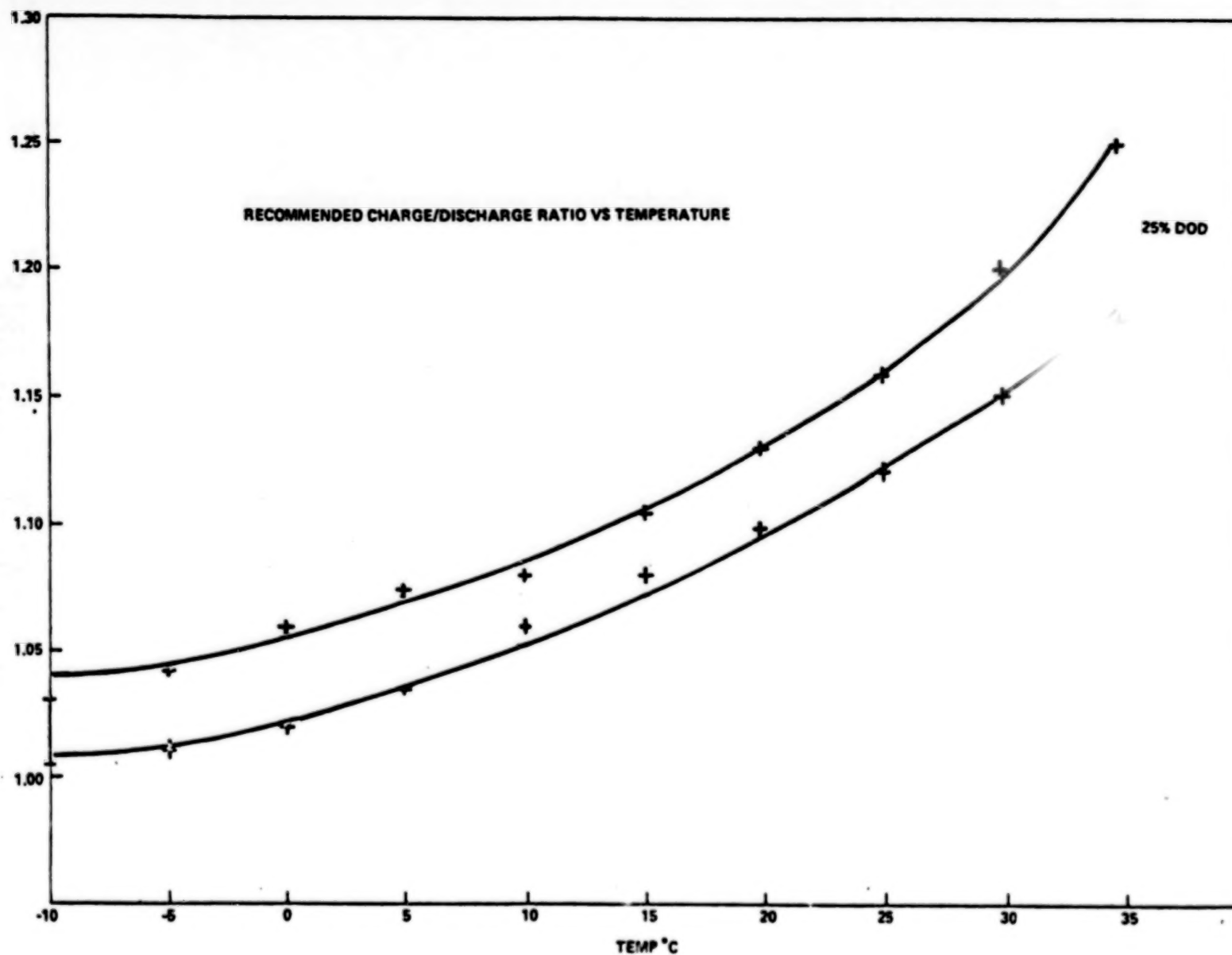


Figure 3 Recommended Charge/Discharge Ratio versus Temperature

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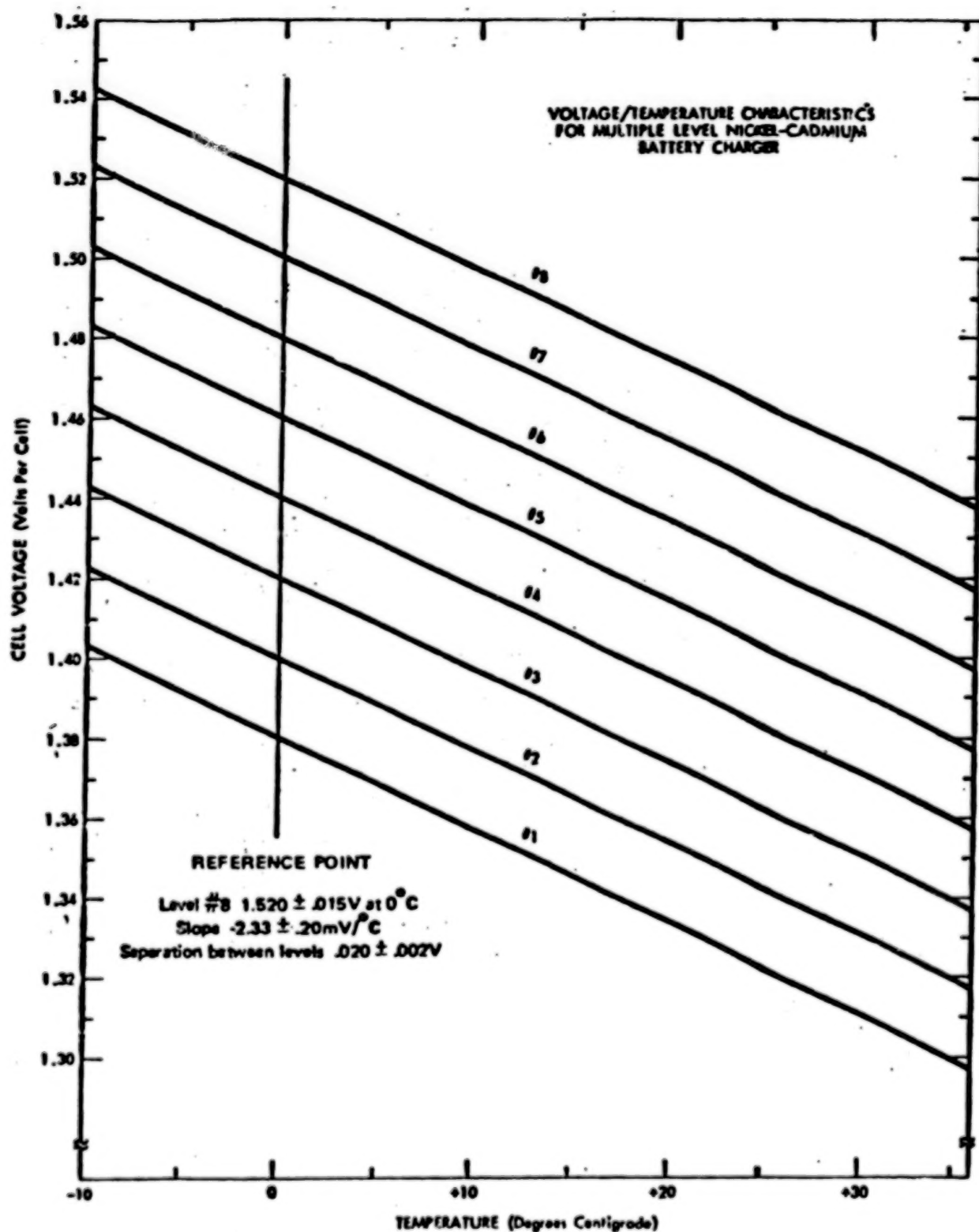


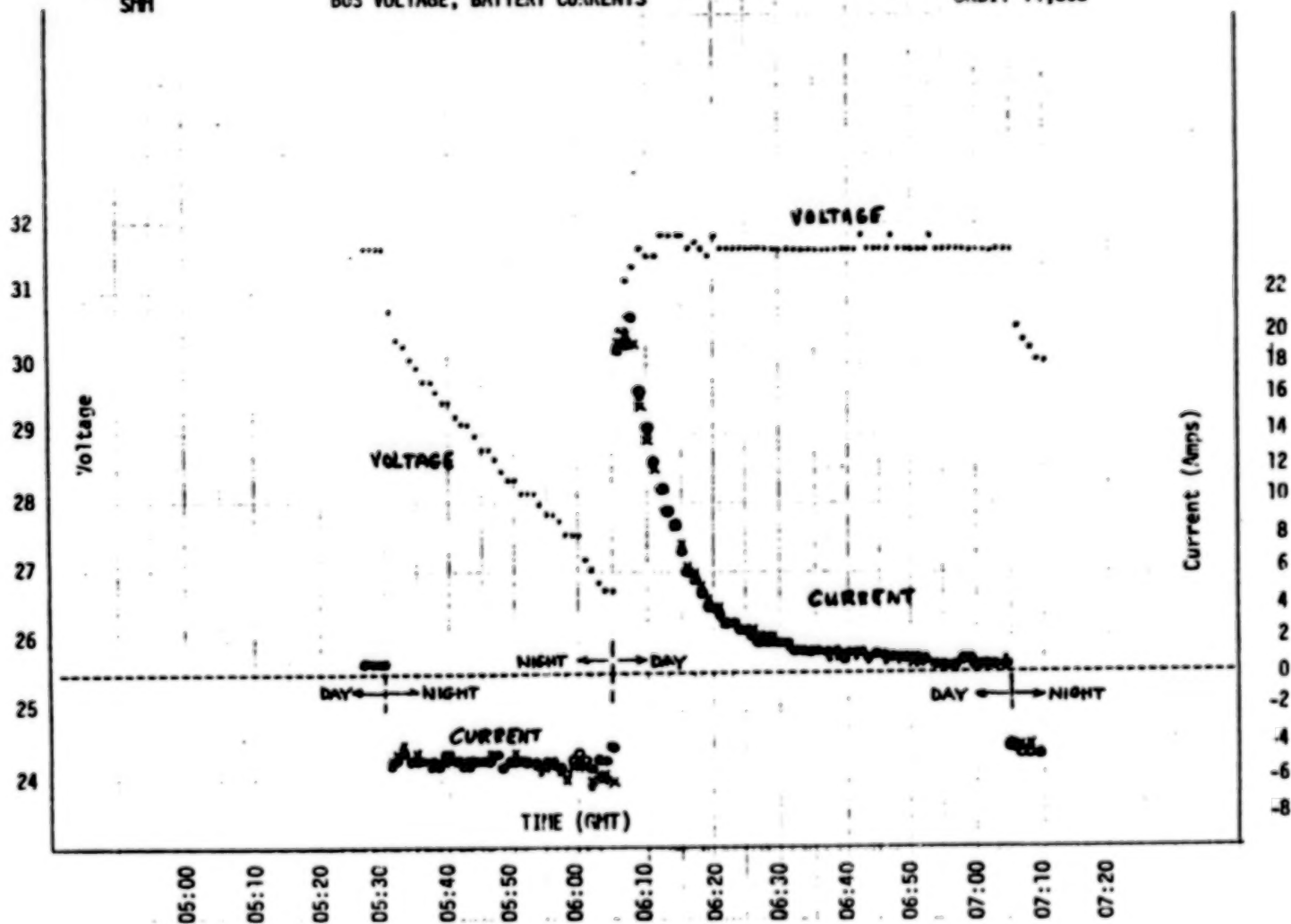
Figure 4. Cell Voltage Limit versus Temperature

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FIGURE 5
SPM

5 mm ORBIT 14058 ab
BUS VOLTAGE, BATTERY CURRENTS

ORBIT 14,858



243

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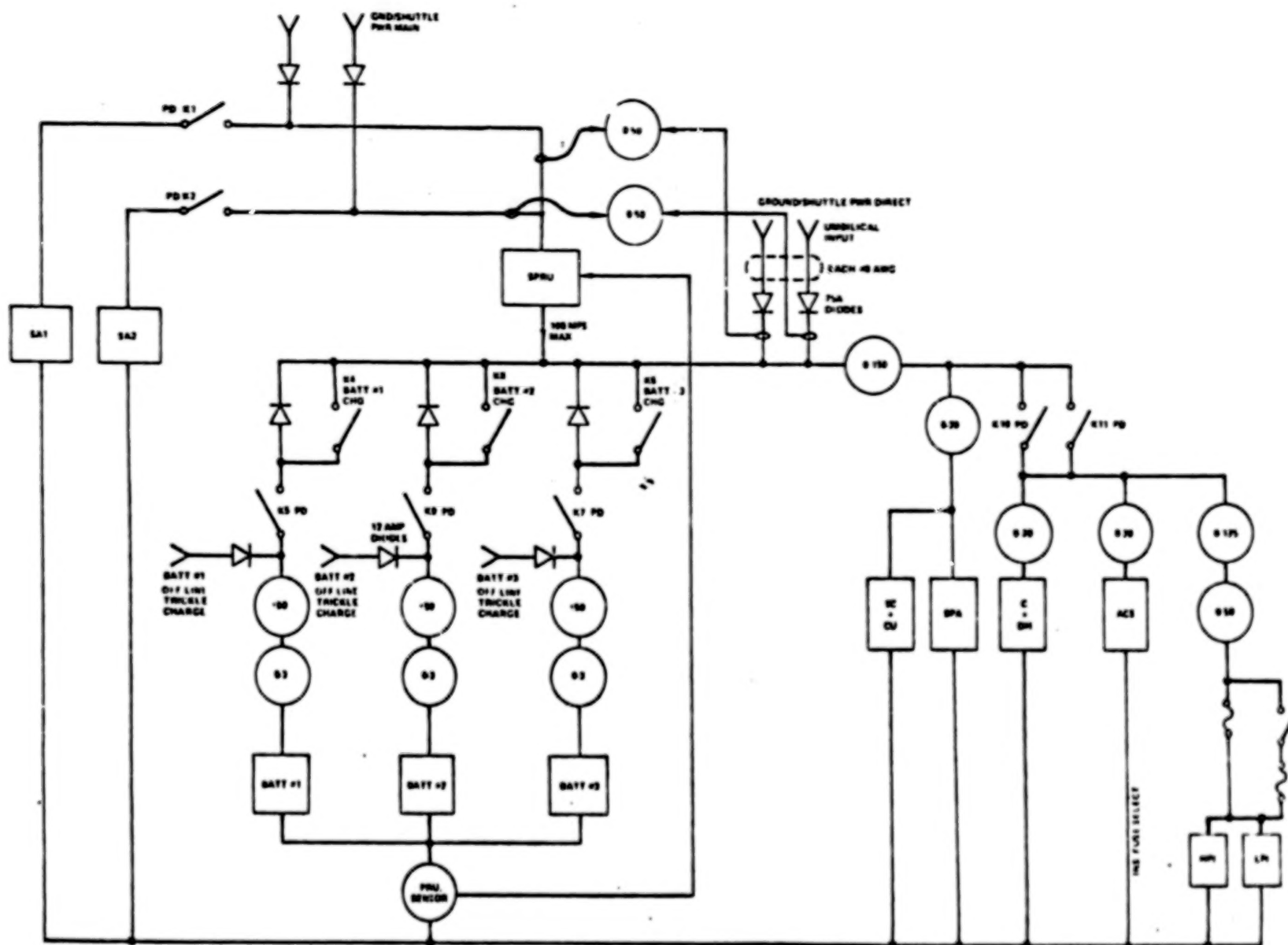
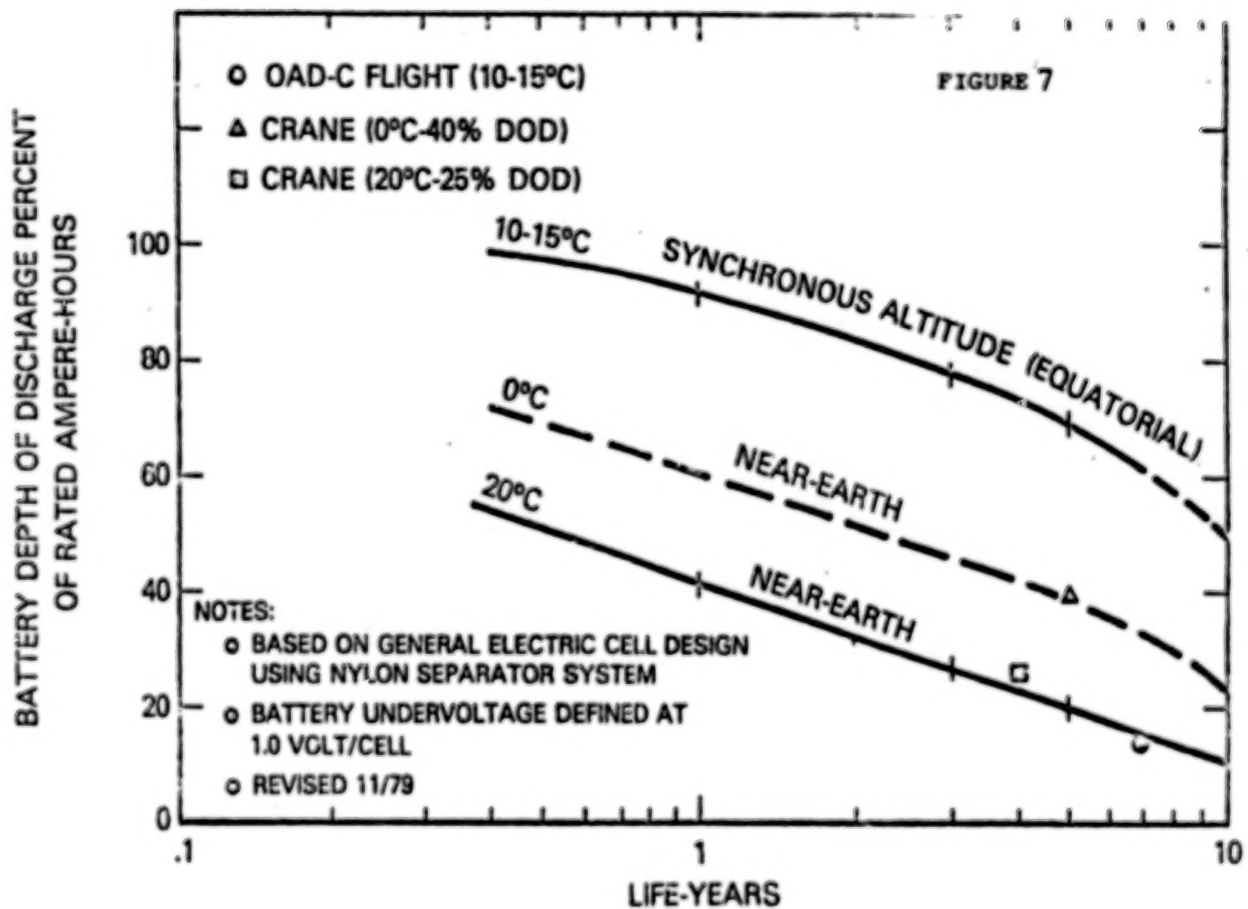


Figure 6 MPS Block Diagram

MAXIMUM DESIGN UTILIZATION
OF NICKEL-CADMIUM BATTERIES
FOR SPACECRAFT APPLICATIONS
(DEMONSTRATED CAPABILITY)



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TABLE III
SIMULATED ERBS CYCLING - NWSC/CRANE
(24 HOURS AT EACH CONDITION - INITIAL ACTIVATION CYCLE)

- BETA 90 - MAX - 2 BAT CASE (48.6M-CHG/48.6M-DISCH)
V_T 5,6,7 at -5,5,15°C
- BETA 65 - MAX - 2 BAT CASE (59M-CHG/38M-DISCH)
V_T 4,5,6 at 5,15,25°C
- BETA 10 - MAX - 2 BAT CASE (Continuous CHG)
V_T 3,4,5 at 5,15,25°C
- BETA 90 - MAX - 1 BAT CASE (48.6M-CHG/48.6M-DISCH)
V_T 5,6,7 at -5,5,15°C
- BETA 65 - MAX - 1 BAT CASE (59M-CHG/38M-DISCH)
V_T 4,5,6 at 5,15, 25°C
- BETA 90 - MIN - 2 BAT CASE (48.6M-CHG/48.6M-DISCH)
V_T 5,6,7 at -5,5,15°C
- BETA 90 - MIN - 1 BAT CASE (48.6M-CHG/48.6M-DISCH)
V_T 5,6,7 at -5,5,15°C
- BETA 90 - MIN - 2 BAT CASE (48.6M-CHG/48.6M-DISCH)
V_T 5,6,7 at -5,5,15°C

246

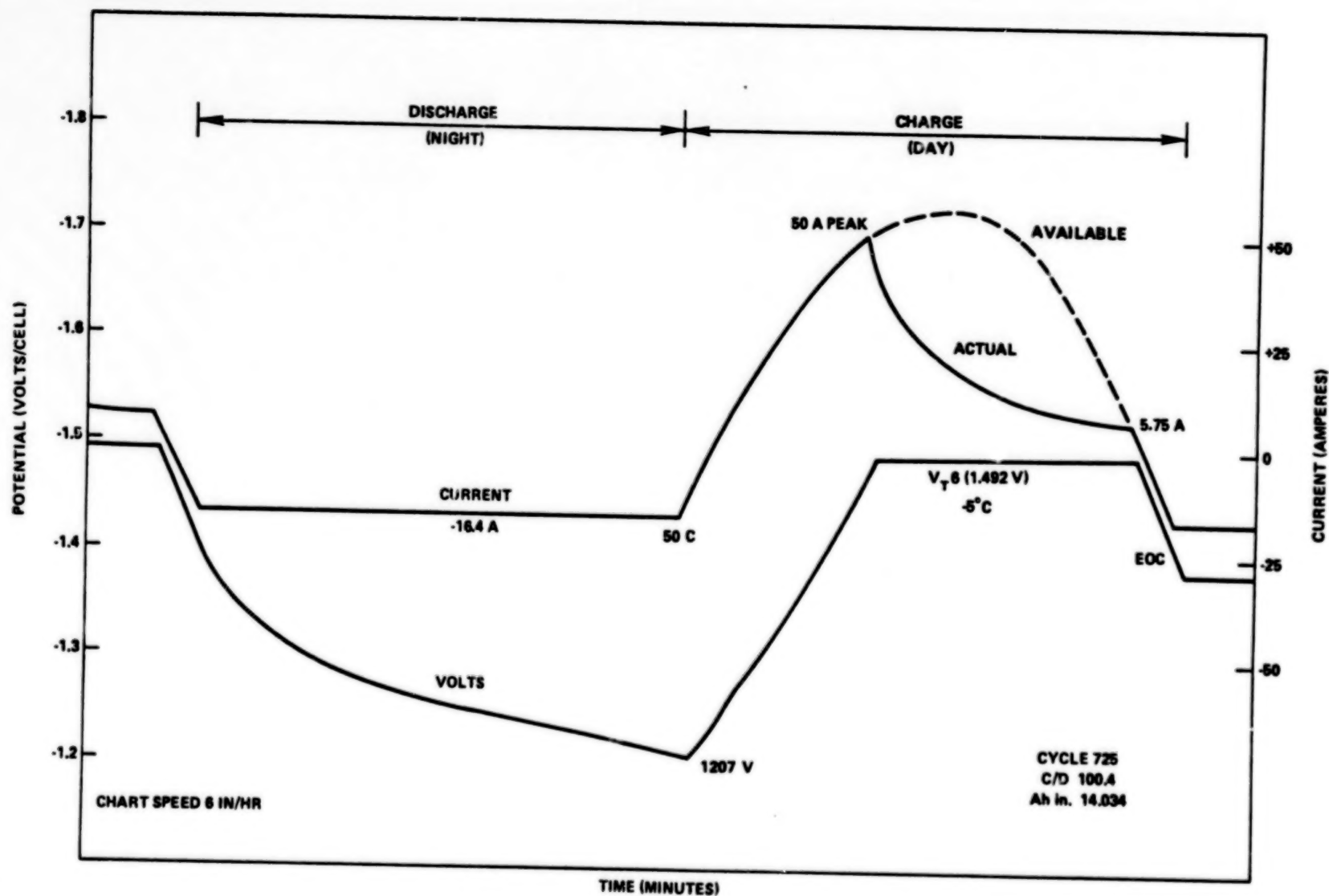


Figure 8 Beta-90 Maximum, One-Battery Case

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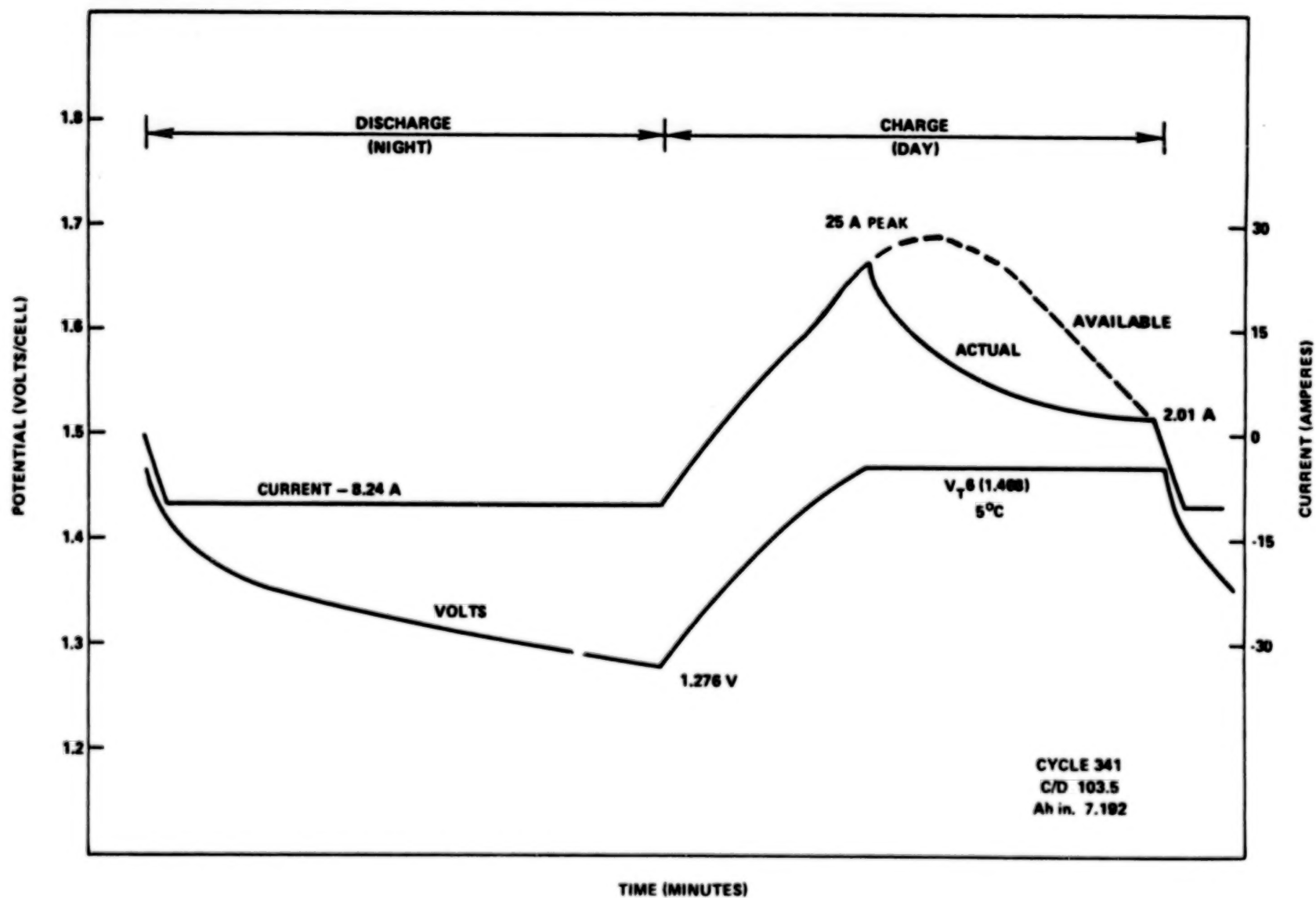


Figure 9 Beta-90 Maximum, Two-Battery Case

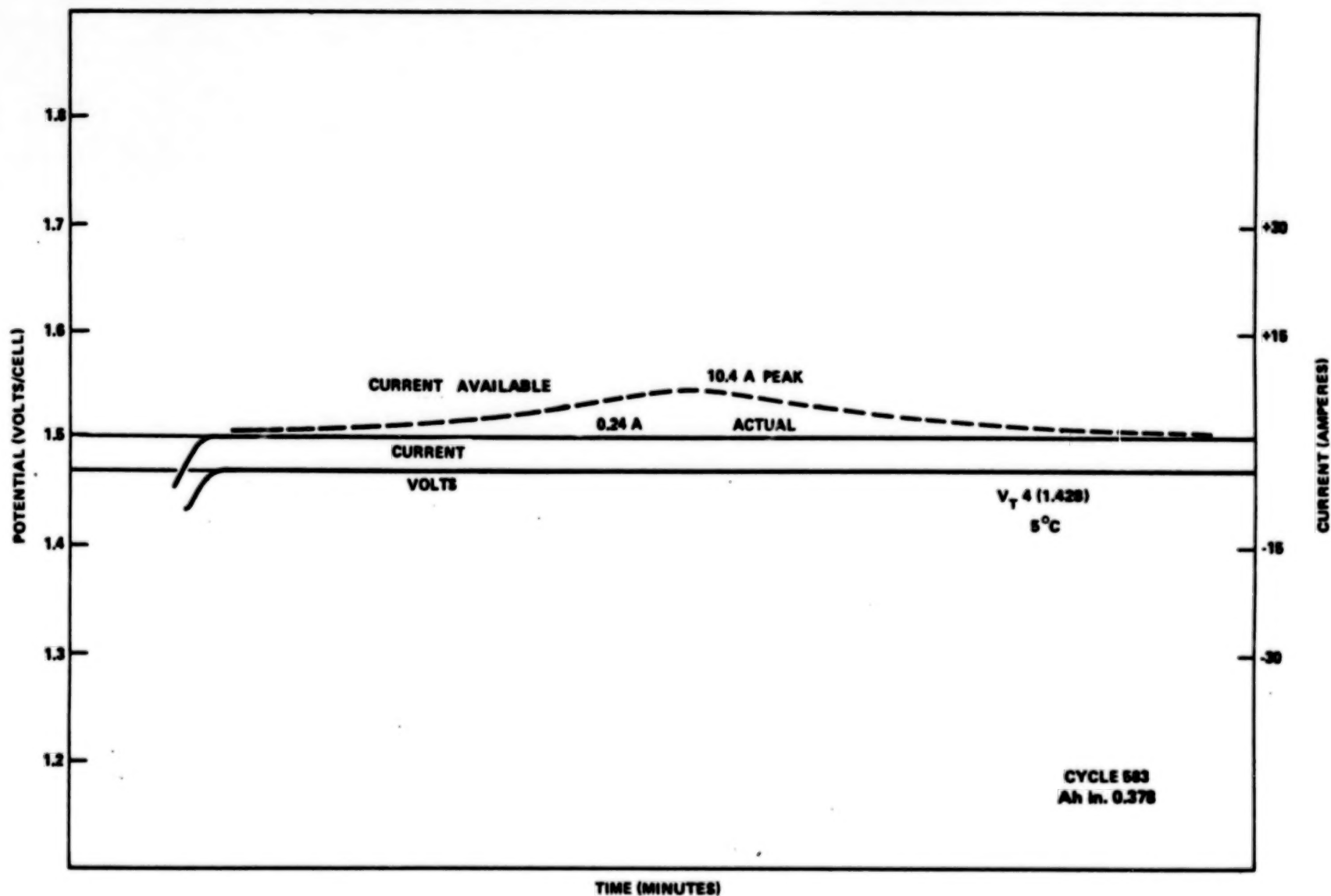


Figure 10 . Beta-10 Maximum, Two-Battery Case

250

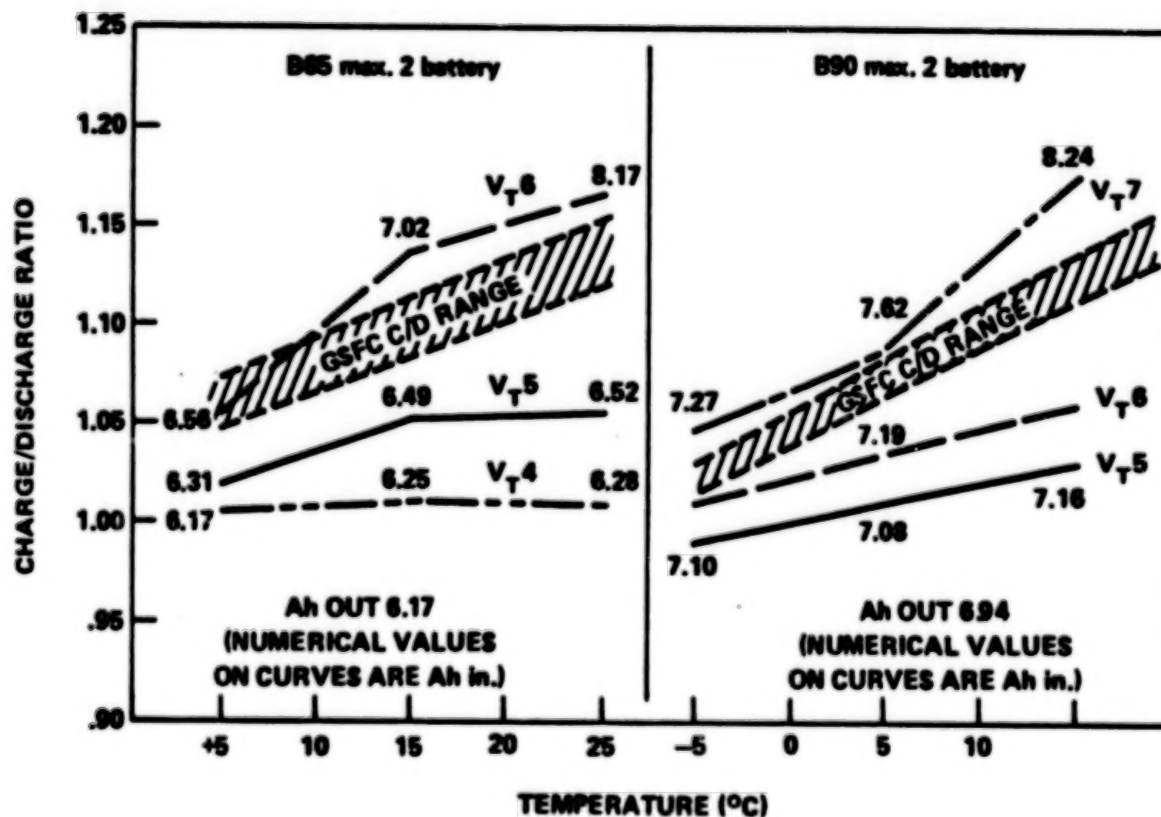


Figure 11 Charge/Discharge Ratio Versus Temperature
(Beta-90 max. - Beta-65 max.)

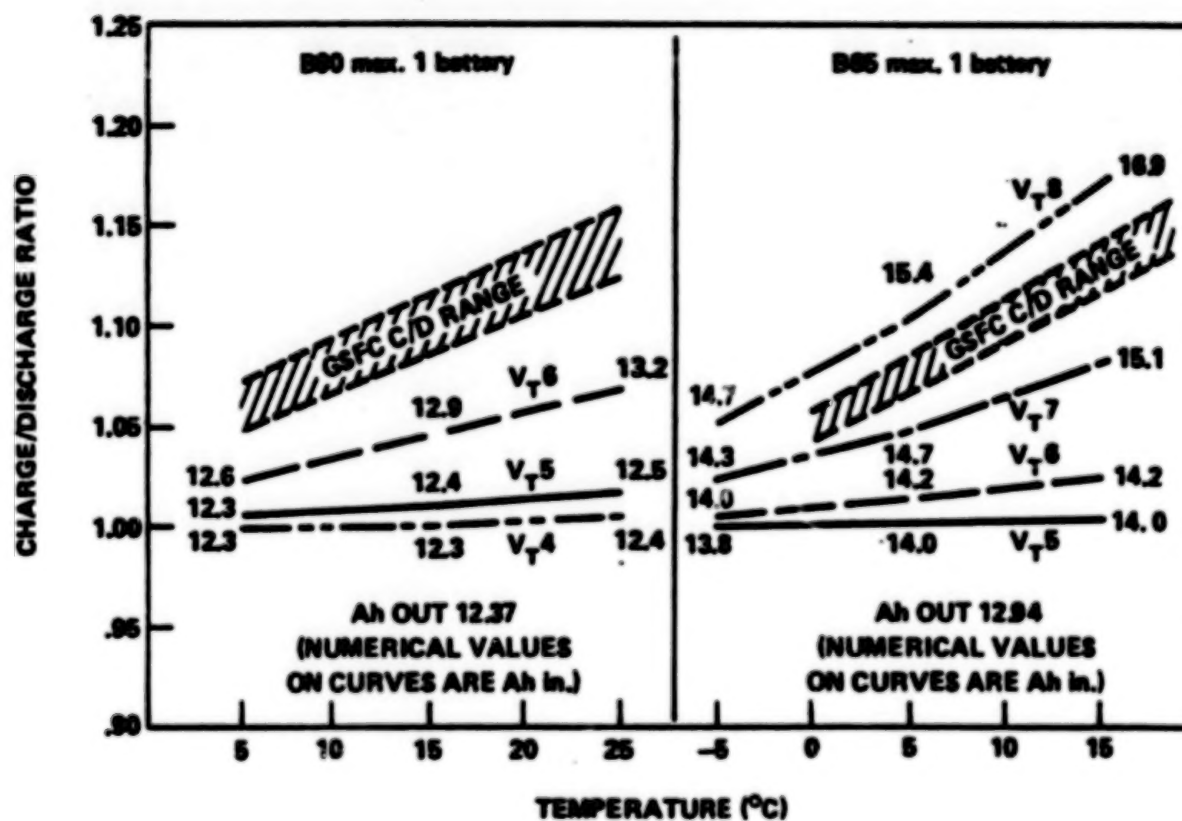


Figure 12 . Charge/Discharge Ratio Versus Temperature (Beta-90 max. - Beta-65 max., One-Battery Case)

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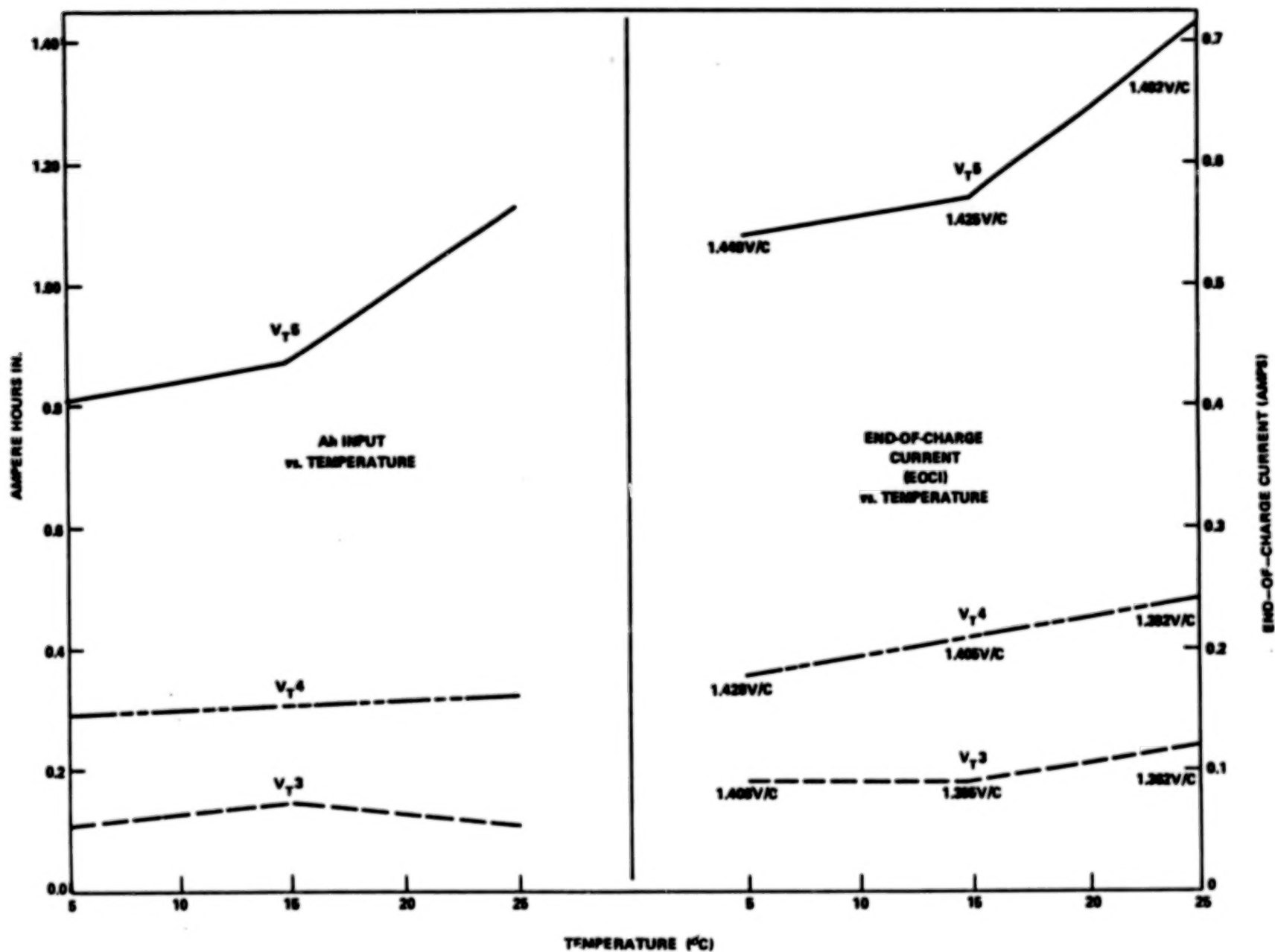


Figure 13 Beta 10, Two-Battery Case

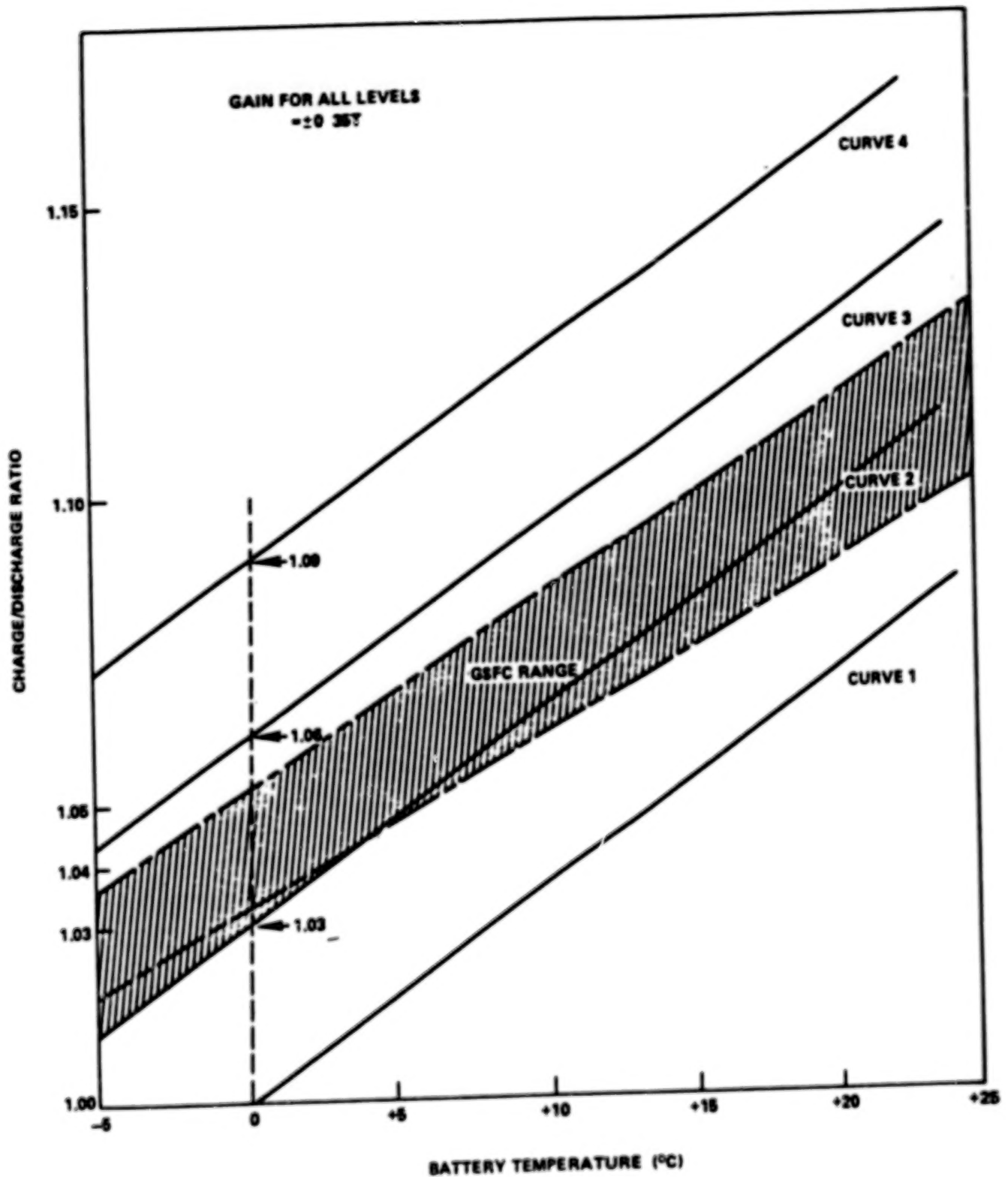


Figure 14 Charge/Discharge Ratio Versus Temperature Limit Curves

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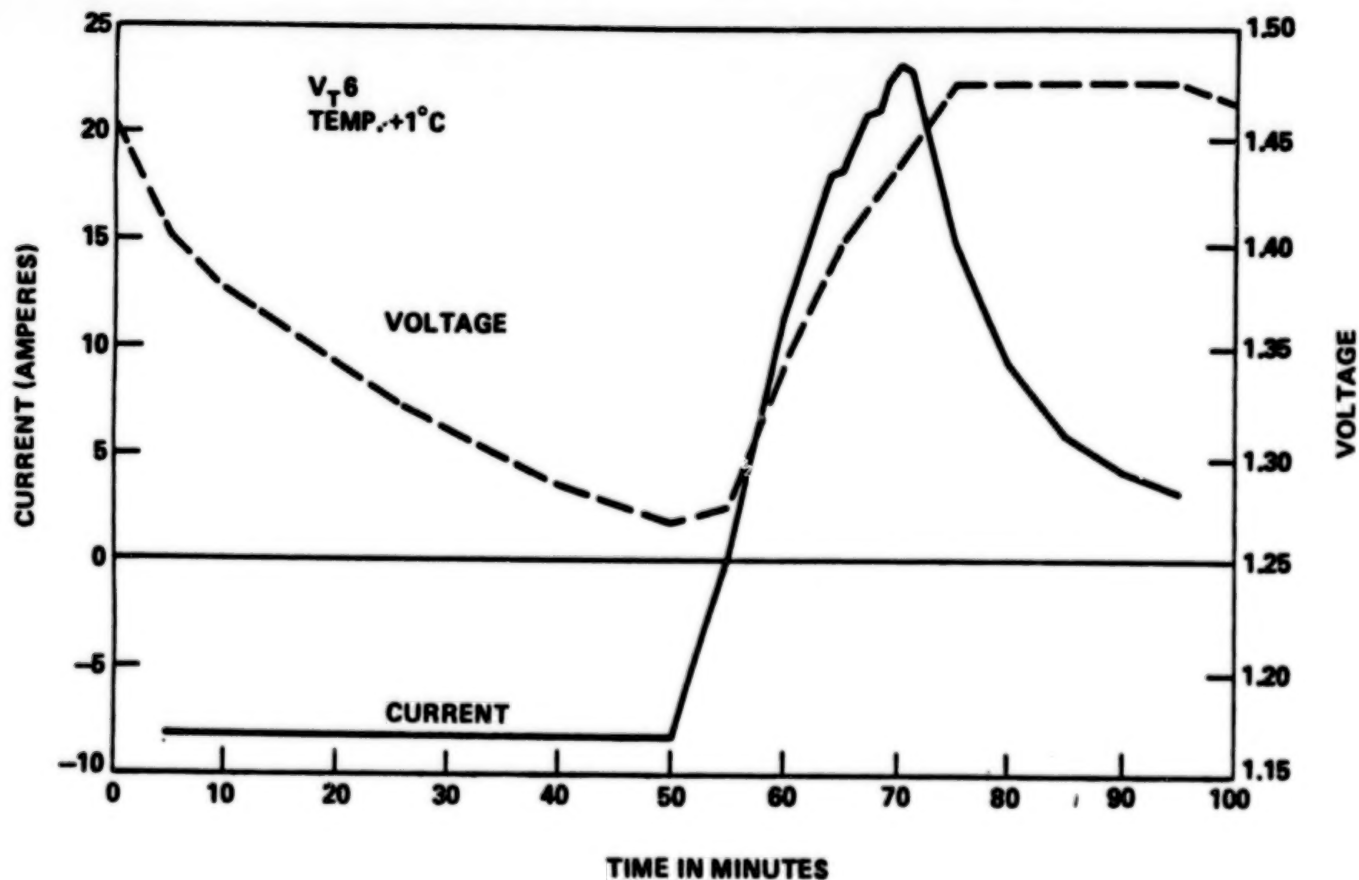


Figure 15 . Beta-90 Beginning-of-Life Profile (Pack 50 E)

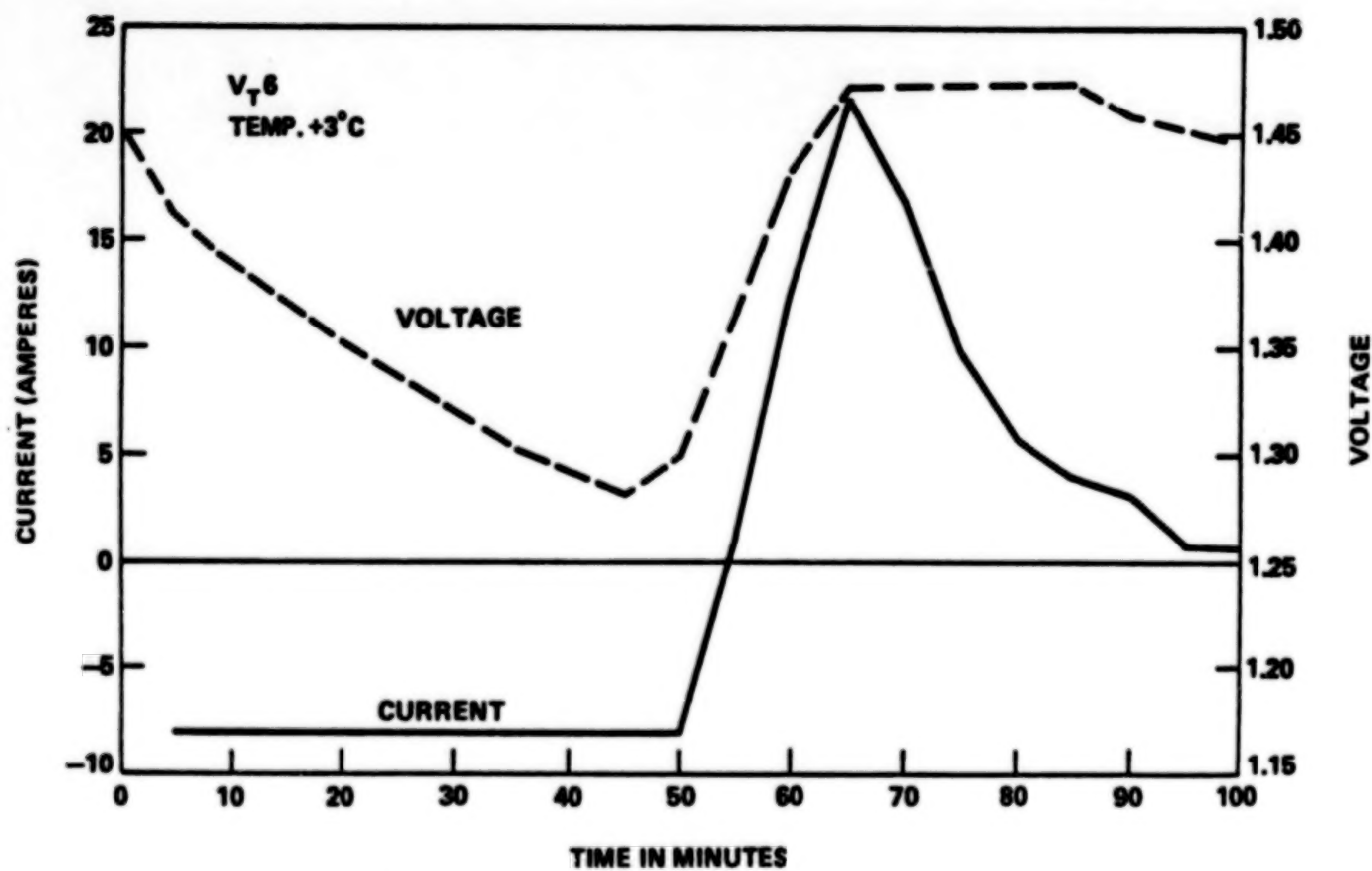


Figure 16' Beta-65 Beginning-of-Life Profile (Pack 50 E)

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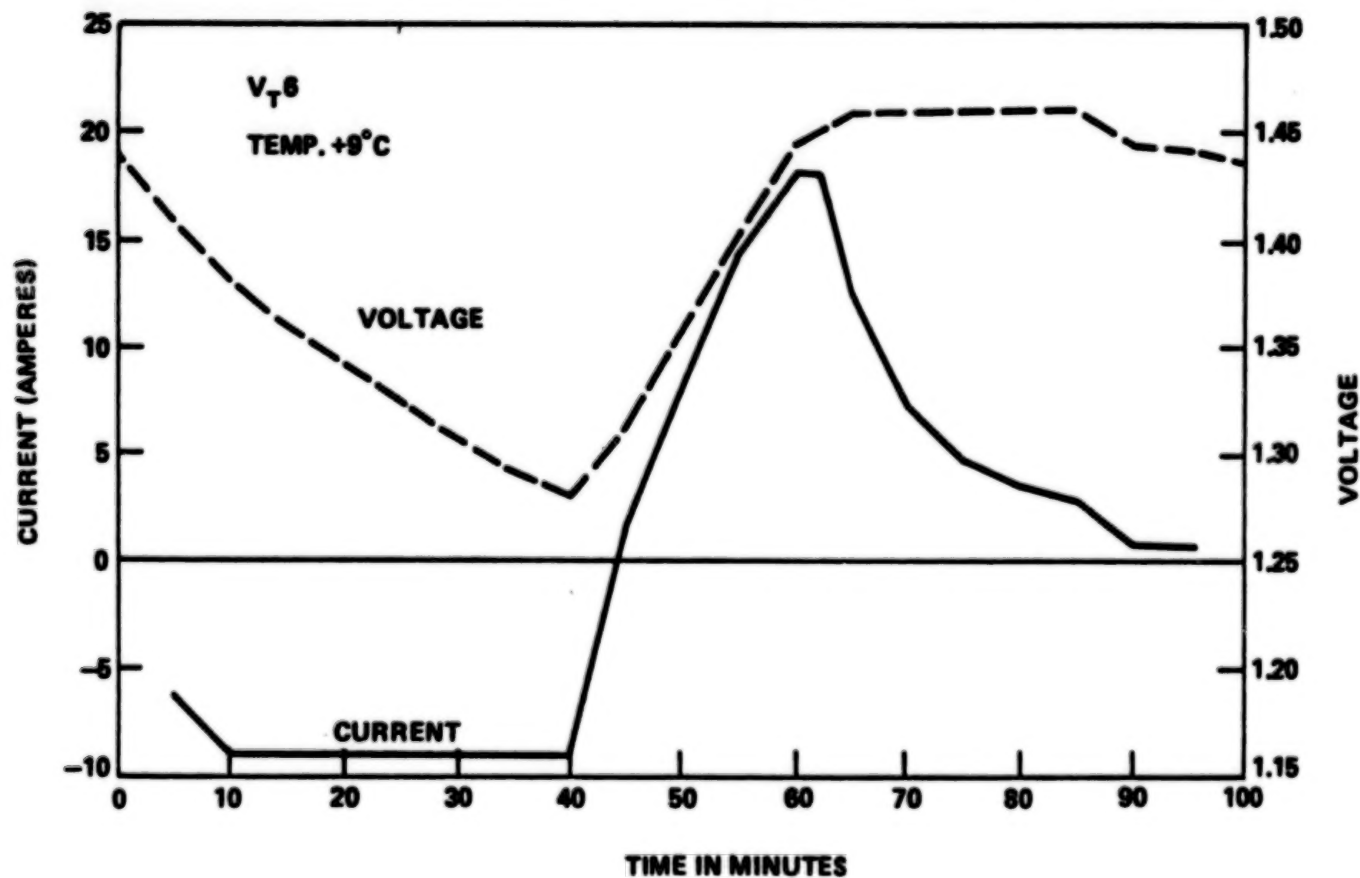


Figure 17: Beta-40 Beginning-of-Life Profile (Pack 50 E)

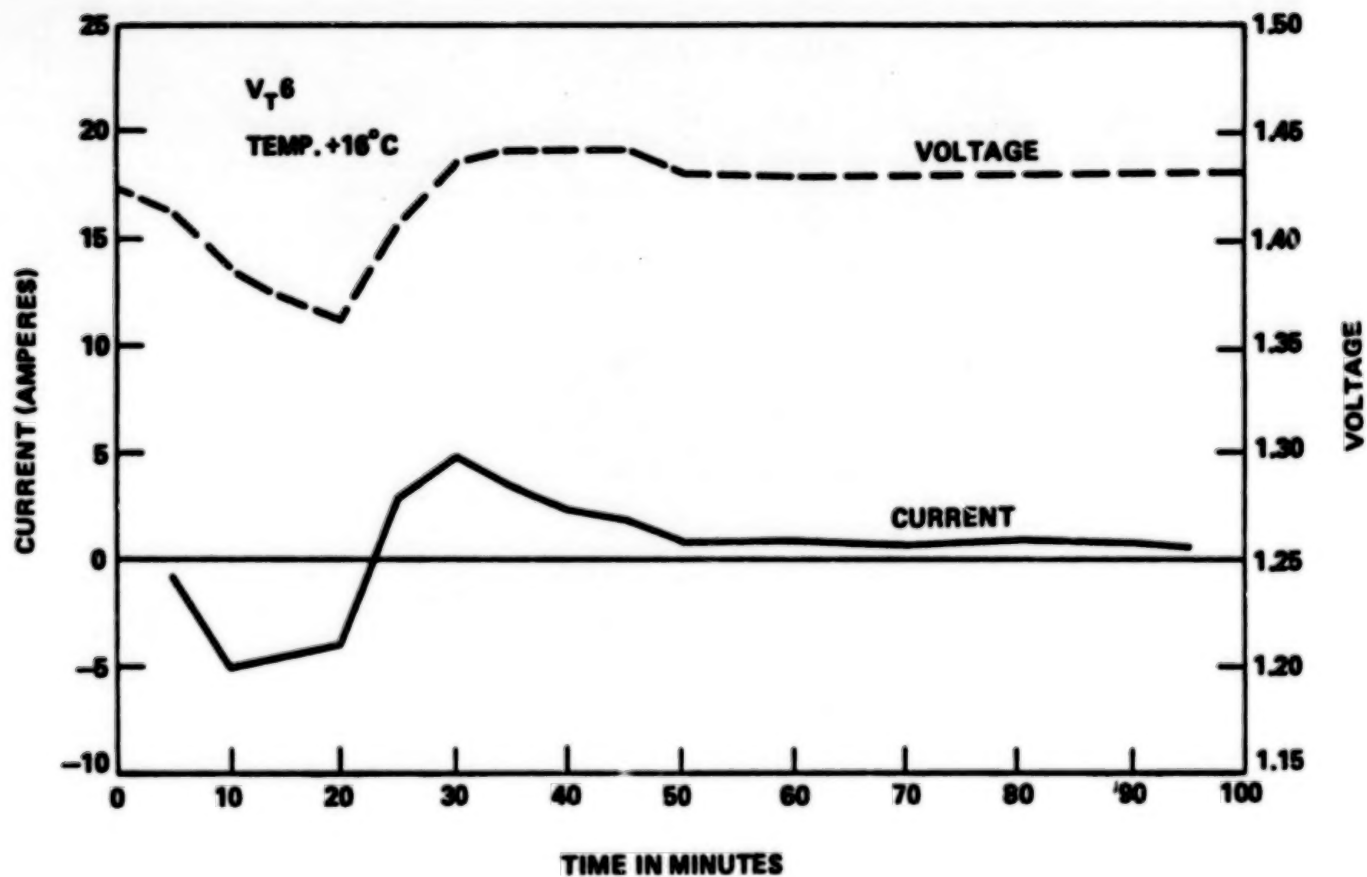


Figure 18 Beta-15 Beginning-of-Life Profile (Pack 50 E)

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Table IV
Quantitative Results of Phase 2 Test

Test Condition	Beta	Temp (°C)	A	Discharge Ah Out	DOD	V _T ⁶	TTVL ¹	Charge TIVL ²	TIVC ³	C/D BTC ⁴	C/D WTC ⁵	C/D WOAHI ⁶
1	90	1	8.23	7.41	14.8	1.477	15	26	-	1.01	1.014	1.014
2	65	3	8.00	6.14	12.3	1.473	13	25	10	1.03	1.055	1.108
3	40	9	8.93	5.66	11.3	1.459	17	25	11	1.06	1.083	1.147
4	15	16	5.00	1.13	2.3	1.443	11	17	50	1.10	1.589	2.321
Beginning-of-Life Simulation												
5	90	1	7.90	7.03	14.1	1.447	18	20	1	1.02	1.025	1.025
6	65	3	8.25	6.40	12.8	1.473	16	24	7	1.03	1.042	1.082
7	40	9	8.58	5.55	11.1	1.459	20	19	11	1.06	1.083	1.175
8	15	16	5.50	2.16	4.3	1.443	20	12	30	1.08	1.236	1.275
End-of-Life Simulation												

- ¹Time to the Voltage Limit
²Time in Voltage Limit
³Time in Trickle Charge
⁴Before Trickle Charge
⁵With Trickle Charge
⁶Without Amp. Hour Integration

BATTERY CHARGE CONTROL

WITH TEMPERATURE COMPENSATED VOLTAGE LIMIT

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General Electric Space Systems Division

ABSTRACT

Battery charge control for orbiting spacecraft with mission durations from three to ten years, is a critical design feature. Starting in 1974, the General Electric Space Systems Division has designed, manufactured and tested battery systems for six different space programs. Three of these are geosynchronous missions, two are medium altitude missions and one is a near-earth mission. All six power subsystems contain nickel cadmium batteries which are charged using a temperature compensated voltage limit. This charging method has been found to be successful in extending the life of nickel cadmium batteries in all three types of earth orbits. Test data and flight data will be presented for each type of orbit.

INTRODUCTION

Secondary batteries, in general, tend to degrade in performance, or "wear out", not from the discharge when they supply energy, but from the charge when electrical energy is fed to the batteries. This is true for lead acid batteries in automobiles and nickel cadmium batteries in spacecraft. The problem is that it is difficult to determine how much electrical energy is necessary to obtain 100% recharge. Too little charge will cause a fairly rapid degradation of discharge capacity; too much recharge will result in a slow degradation of performance, mainly caused by temperature effects on plates and separators. In automobiles, the voltage regulator has become a very effective method of extending battery life. In spacecraft, using nickel cadmium batteries, the temperature compensated voltage limit has also shown to be an effective method of extending battery life.

POWER SUBSYSTEM DESIGN

In designing spacecraft power subsystems, the battery charge control is considered the most critical feature for providing reliable long life energy storage. At the General Electric Space Systems Division, six different power subsystems have been designed, manufactured and tested during the past eight years. Four of these programs have spacecraft in earth orbit, and two are scheduled for launch within the next few years. Although the space missions include geosynchronous orbits, medium altitude orbits and near earth orbits,

all battery control is regulated by temperature compensated voltage limits. The six power subsystems are not identical, but do have many common features. All subsystems have:

- Direct energy transfer from solar array to loads.
- A regulated power bus.
- Three sixteen cell nickel cadmium batteries.
- Redundant boost regulators between the batteries and the bus.
- Heaters and thermostats on all batteries.
- Independent charge regulators for each battery having a maximum current limit and four selectable temperature compensated voltage limits.

TEMPERATURE COMPENSATED VOLTAGE LIMITS

The battery charge regulators are designed such that when battery voltage reaches the limit for the specific battery temperature, the current automatically adjusts to maintain the voltage. Charging is not terminated, nor is there a switch to a lower charge current. The design of the voltage limit curves is, of course, of great importance. Figure 1 is an example of the V-T (voltage-temperature) curves used for several programs. These curves must be tailored to the voltage-temperature characteristics of the specific nickel cadmium cells that are used in the batteries. For each power subsystem, it is necessary to perform battery charging tests to determine the relationship between battery voltage, temperature and current. At constant temperature, the nickel cadmium cell voltage will be a direct function of the logarithm of the current. This "Tafel" relationship is shown on Figure 2.

After the Tafel curves have been determined, the V-T curves can be designed to meet whatever criteria satisfy the mission requirements. The size of the heaters and the size of the radiators can be established. The heaters must be of sufficient wattage so that their heat plus battery dissipation will maintain the minimum battery temperature, typically 0 C. The radiator size must be of sufficient size so that it can radiate the maximum battery dissipation and limit the maximum battery temperature, typically 20 C.

GEOSYNCHRONOUS ORBIT

Two of the three geosynchronous programs have spacecraft in orbit. Figures 3 and 4 present the battery data for one simulated orbit in the laboratory, and one actual plotted from flight telemetry. The laboratory test

is at 60% depth of discharge at 20°C, and the flight orbit is at 50% depth of discharge at 11°C. The greatest significance is that the battery temperature is maintained almost constant. The charge control will compensate not only for temperature, but will automatically adjust itself for varying depth of discharge.

MEDIUM ALTITUDE ORBIT

One of the two medium altitude programs has several spacecraft in orbit. Figures 5 and 6 present the battery data for one simulated orbit in the laboratory, and one actual orbit plotted from flight data. The laboratory test is at 60% depth of discharge at -2°C, and the flight data is at 22% depth of discharge at +2°C. This was not a maximum eclipse orbit. Again, the temperatures are very uniform, not varying more than three degrees from the average, and the charge control adjusts for the difference in depth of discharge.

LOW ALTITUDE ORBIT

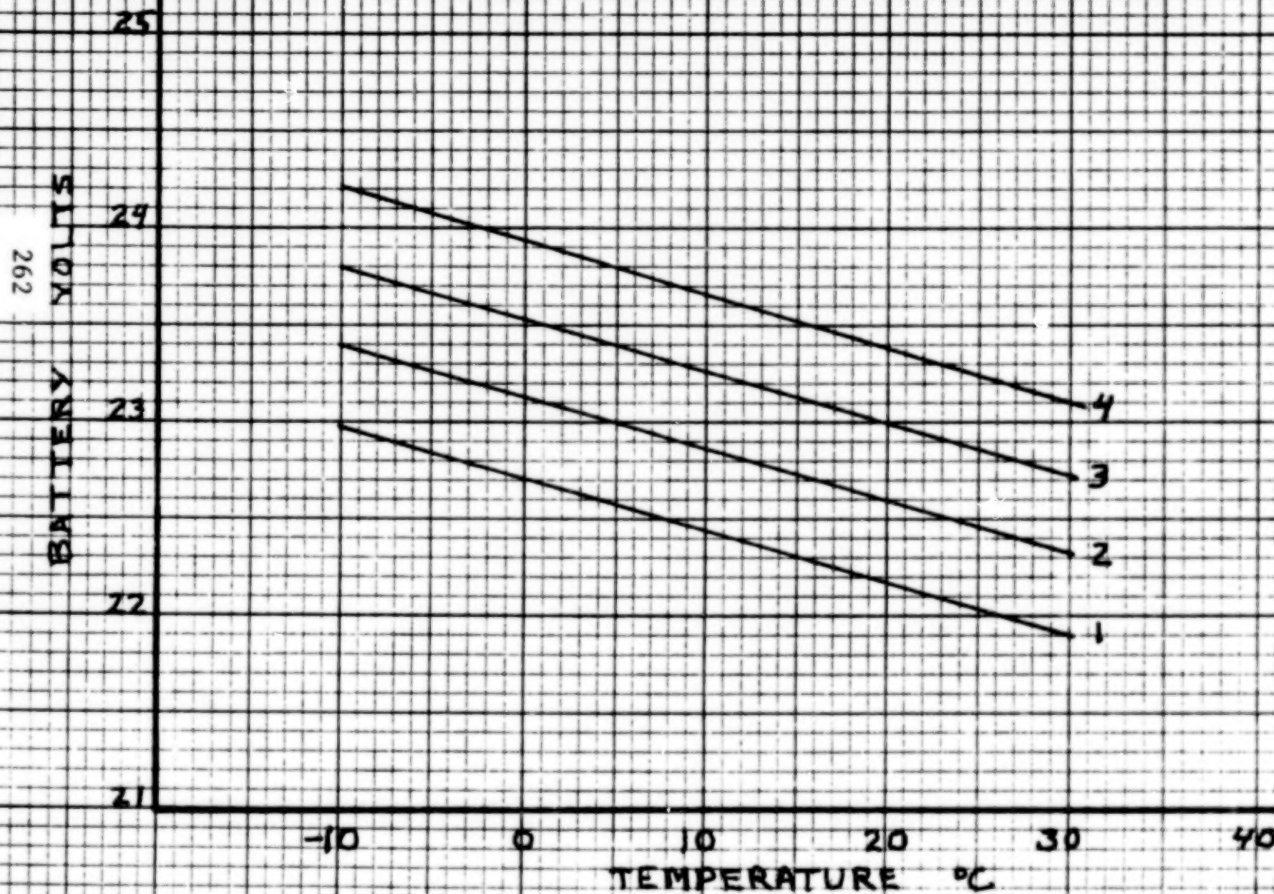
The one low altitude program spacecraft is in orbit. Figures 7 and 8 present the data for one simulated orbit in the laboratory, and one actual orbit plotted from flight data. The laboratory test is at 16% depth of discharge at 10°C, and the flight data is at 10% depth of discharge at 15°C. With the 105 minute orbit, the battery charge current does not actually reach a steady state value as long as there are eclipse periods. However, when the spacecraft enters a period of no eclipses, the battery charge control will automatically continue to reduce charge current and prevent temperature rise.

SUMMARY

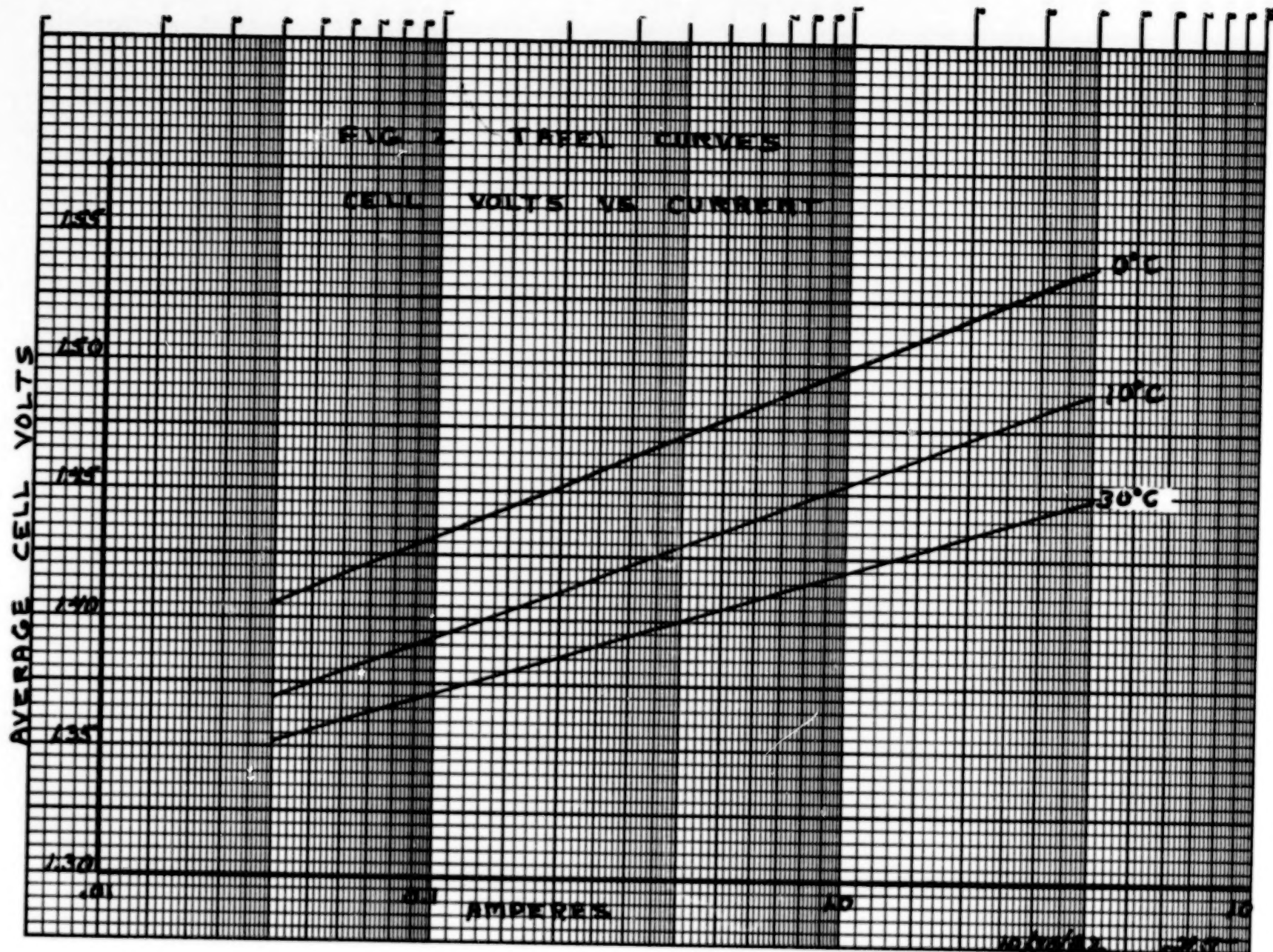
Battery charge control with temperature compensated voltage limit, has been found to be satisfactory for space power subsystems in geosynchronous, medium altitude, and low altitude spacecraft.

FIG 1 - BATTERY VOLTAGE LIMITS

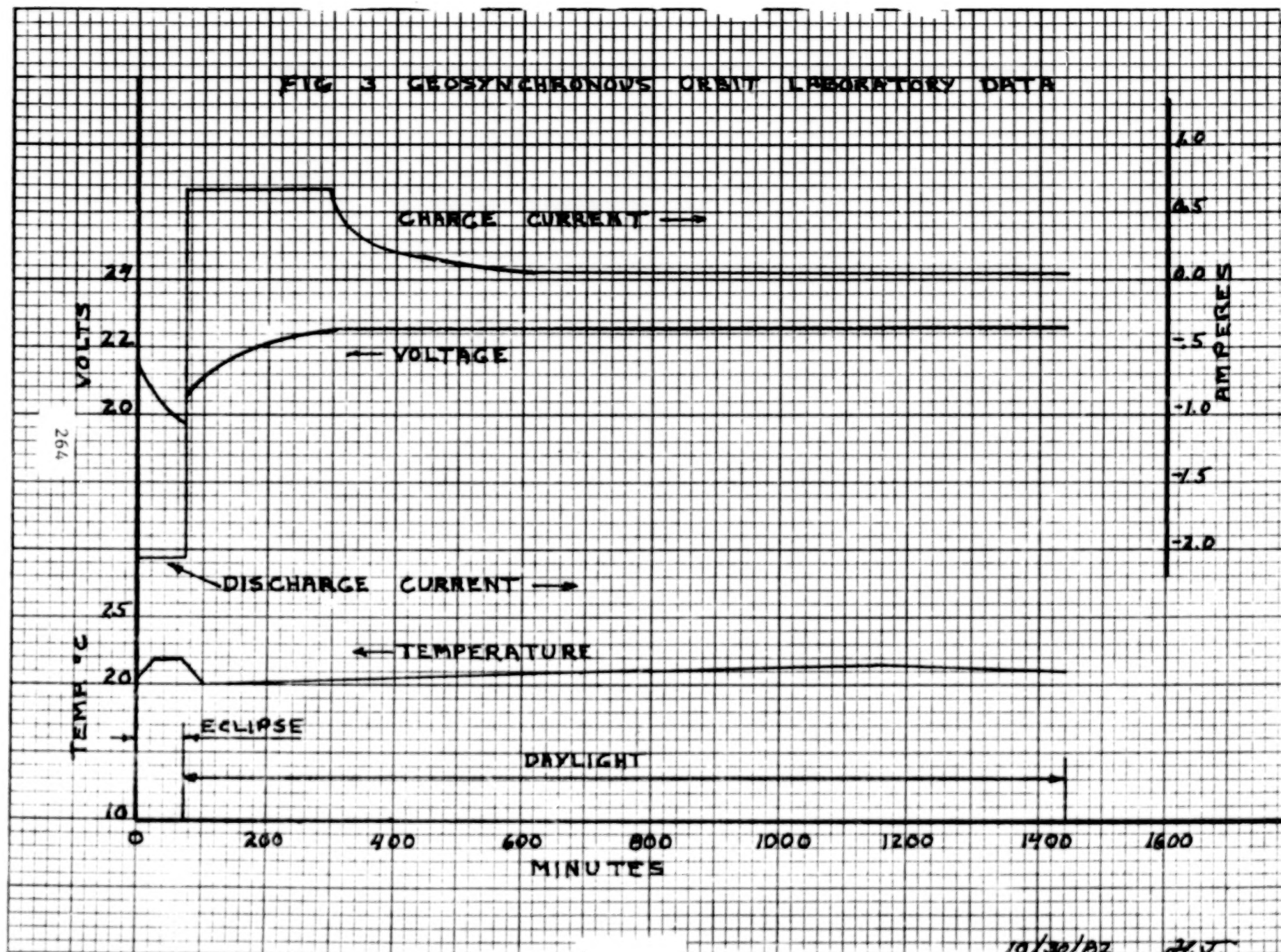
VOLTAGE VS TEMPERATURE

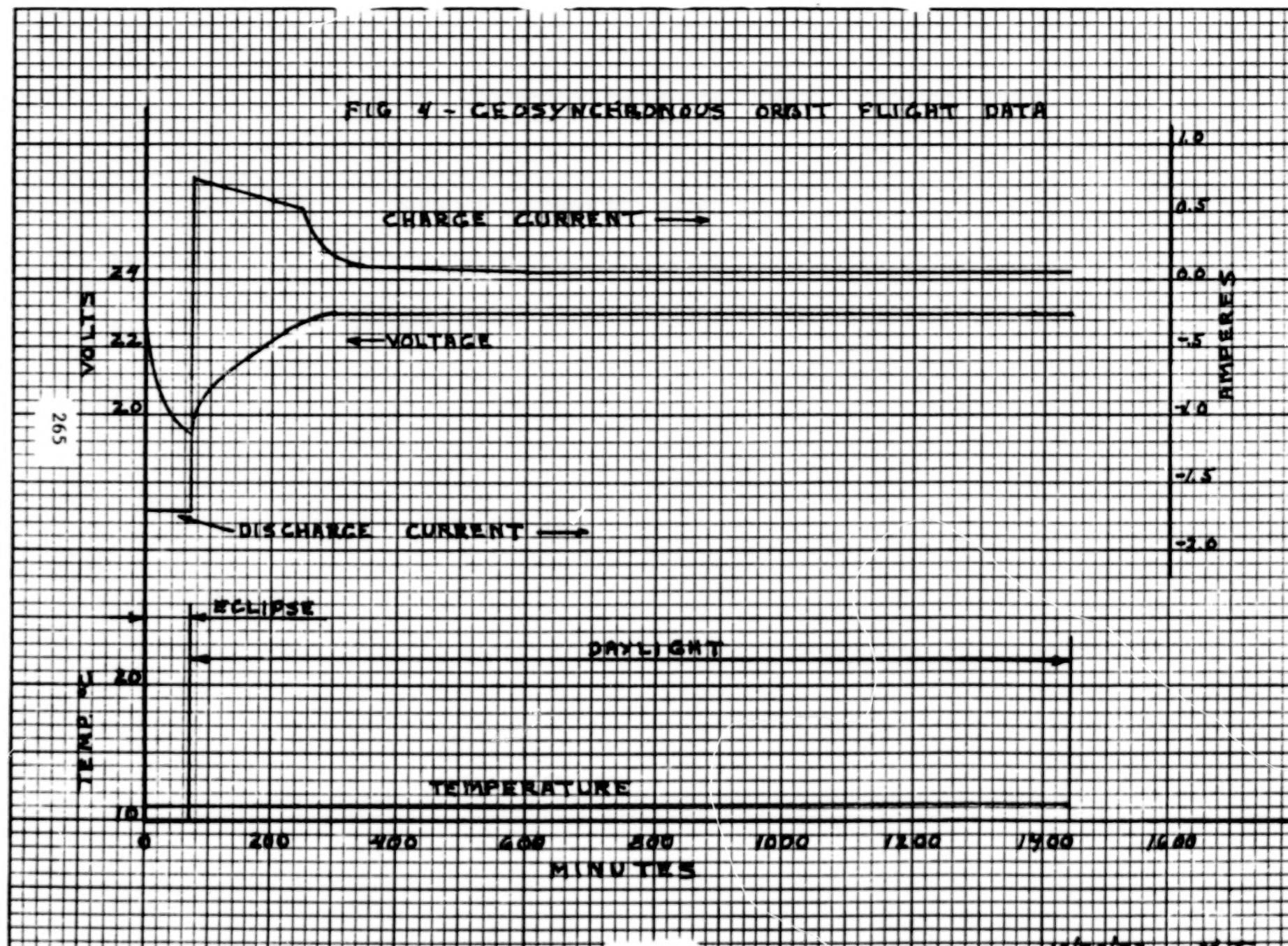


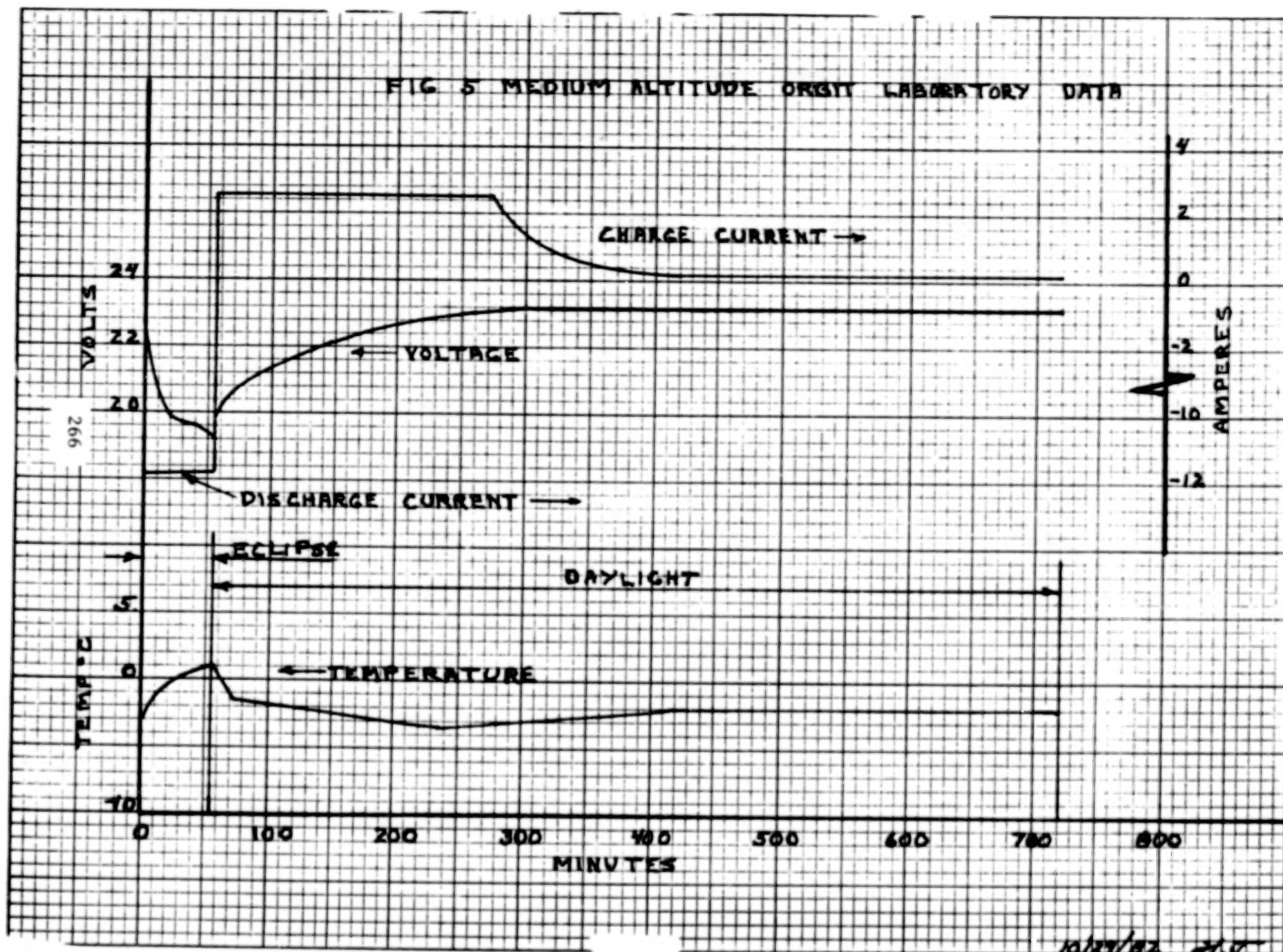
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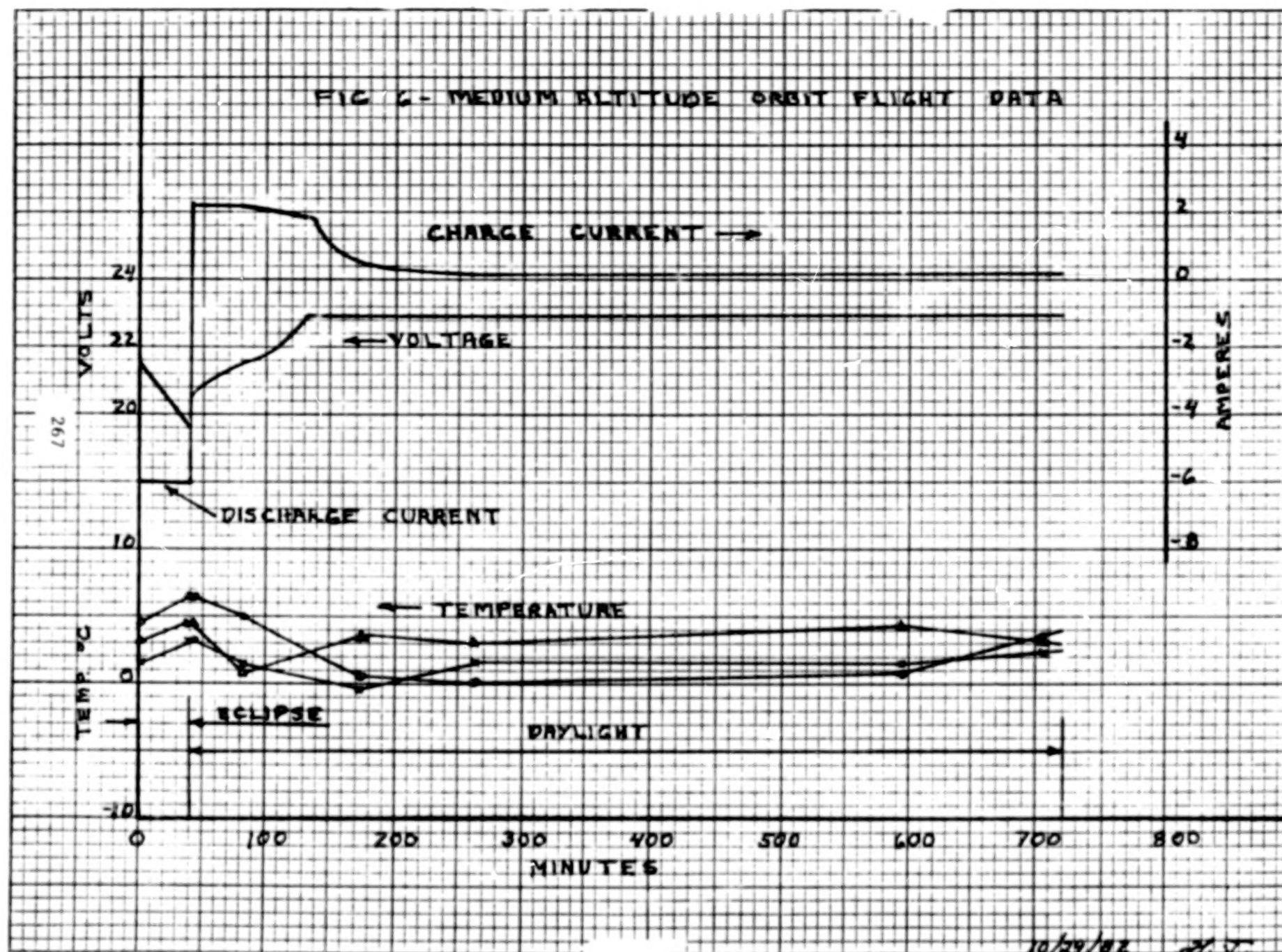


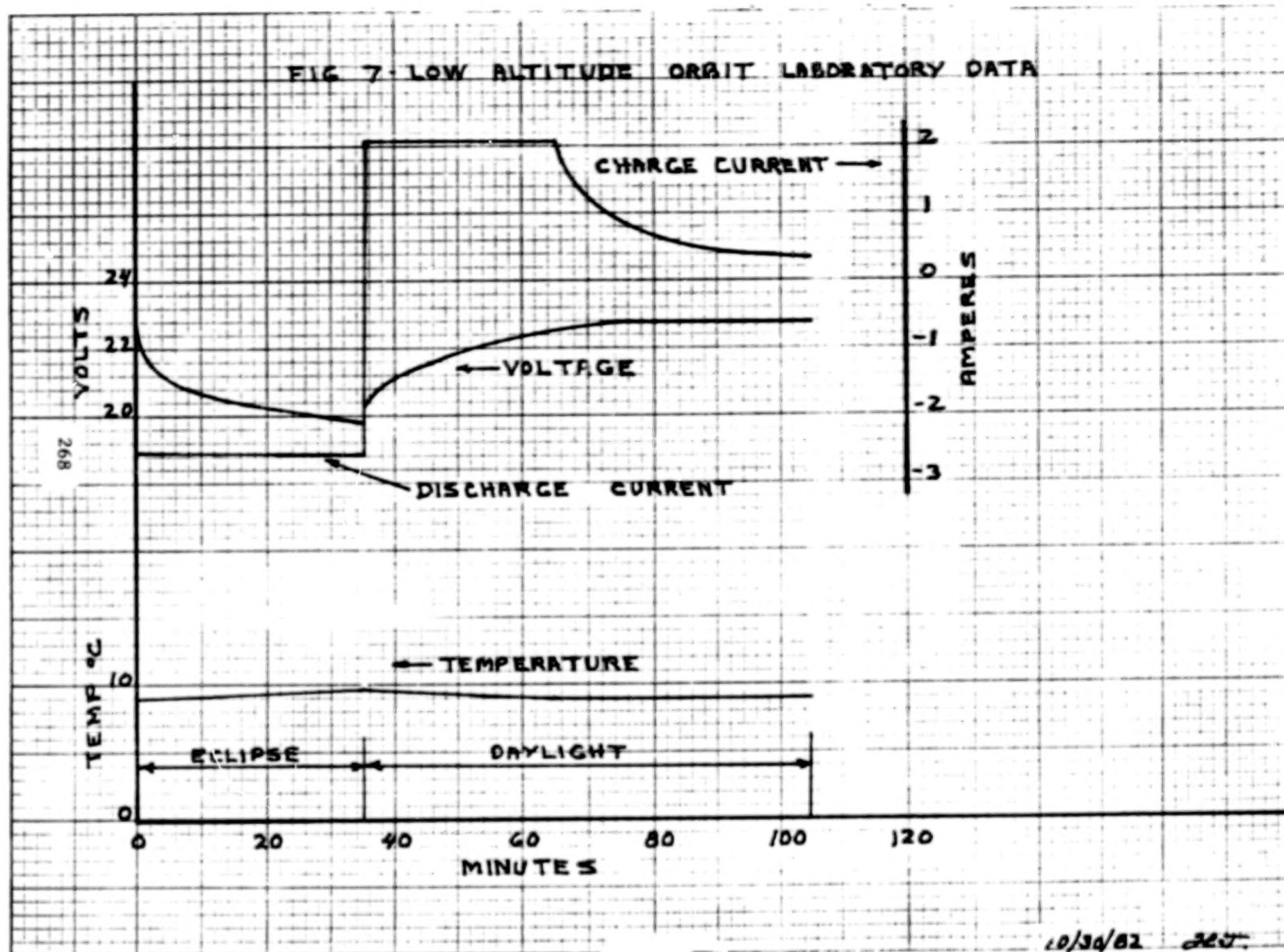
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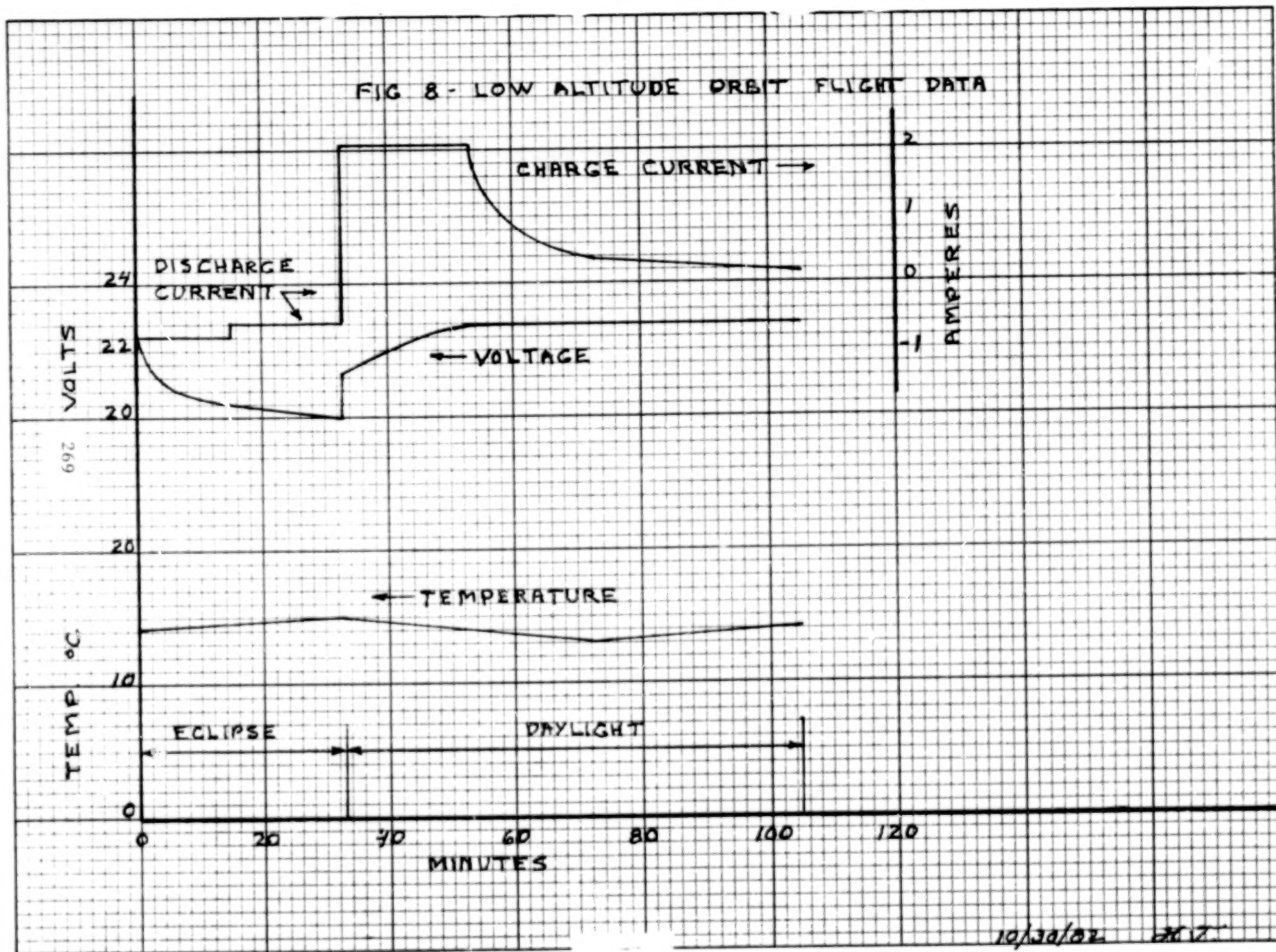












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CONTROL REQUIREMENTS FOR FUTURE BATTERY SYSTEMS

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Denver, Colorado

ABSTRACT

Sophisticated battery control systems are required to support the high power, high energy spacecraft secondary battery systems of the post 1985 time period. Four categories of battery control system functions are defined and discussed: Battery Operational Control, Auxiliary System Control, Battery System Status Indication and Fault Detection/Fault Isolation. A concept for implementation of such a control system is also presented and discussed.

INTRODUCTION

The vast majority of spacecraft secondary batteries flown in the 1970's were low voltage (28 volt or less) Nickel-Cadmium (Ni/Cd) systems in applications rated at 3kW or less. The only active battery control function needed was charge control. Battery discharge control, to a large extent, was accomplished by spacecraft design with depth-of-discharge (DOD) limited to less than 25% for most LEO applications. This was possible because load profiles were relatively simple, predictable and repetitive. Other battery control functions, such as reconditioning, were handled via ground control. Battery system status was not a critical requirement, again because of the repetitive, predictable load profiles and the fact that system design guaranteed sufficient energy available on each orbit to recharge the battery.

The battery charge control techniques, developed and refined over two decades for the Nickel-Cadmium system also apply, to a great extent, to Nickel-Hydrogen (Ni/H₂) systems. These techniques take maximum advantage of the overcharge tolerance of the aqueous Nickel systems to insure all cells are charged fully and equally.

In the future, increasing power requirements together with mass and volume limitations will move us toward higher performance battery systems: systems with higher voltage and higher capacity and systems with chemistries quite different from Nickel-Cadmium and Nickel-Hydrogen. This means operation at deeper DOD's and operation with highly variable load profiles.

These high performance battery systems will require active control systems in addition to basic charge control. This paper presents some

preliminary functional requirements for advanced battery control systems and describes a conceptual implementation of such a control system.

PROJECTED BATTERY SYSTEM CHARACTERISTICS

The initial, and perhaps obvious, requirement of post 1985 spacecraft battery systems is higher power and higher energy capability. There is general agreement that power systems capable of 5kW to in excess of 100kW will be required in this 1985-2000 time period (ref. 1, 2 and 3). As shown in figure 1, these power levels require energy storage capabilities ranging from 3kW-hr. to 60kW-hr. for LEO applications and even higher for GEO applications. In addition to the power and energy requirements, power system design considerations are leading to higher voltage distribution. Batteries as high as 300 volts have been proposed requiring over 200 series connected cells.

These power-energy-voltage requirements result in batteries that are not only larger in terms of mass and volume than batteries of the 1970's, but also more complex. More cells in series are required to meet voltage requirements and more batteries in parallel are needed to meet power and energy requirements. Figure 2 illustrates this complexity in terms of total number of battery cells required for systems requiring up to 60kW-hrs of energy storage. A comparison between the existing NASA Modular Power System (MPS) design and a conceptual design for RADSAT further illustrates this point. A full power MPS contains 3, 22 cell 50 ampere-hour, Ni/Cd batteries for a total of 66 cells. The conceptual battery design for RADSAT, ref. 4, contains 600, 110 ampere-hour Ni/H₂ cells.

Spacecraft battery systems of the 1970's were predominantly Nickel-Cadmium. Nickel-Hydrogen systems are now coming into service and may become the predominant battery of the 1980's. Higher energy density batteries such as Lithium-Metal Sulfide, Sodium-Sulphur and Zinc-Bromine have been suggested (ref. 3) as energy storage options for the 1990's and beyond. This variety of battery types can present us with mechanical, thermal and electrical characteristics quite different from the 28 volt Ni/Cd battery system of today.

Future battery systems may grow to encompass more than just battery cells or modules. Advanced batteries such as the Zinc-Bromine require electrolyte storage and flow control. The high temperature Lithium-Metal Sulfide and Sodium-Sulfur batteries may require active thermal control to maintain operating temperatures and to control freeze and thaw cycles. Even the high power Nickel-Cadmium and Nickel-Hydrogen batteries may require active thermal control. These auxiliary functions further add to overall battery system complexity and control requirements.

Autonomous operation will be a key requirement for these future batteries. The need for autonomy is driven by two factors: The complexity of the battery itself; and the higher level requirement for power system and

spacecraft autonomy. The need for power system automation for both NASA and DOD missions has been discussed in numerous papers (ref. 1, 5 and 6) and include benefits in areas of cost, operational flexibility, and survivability.

BATTERY CONTROL SYSTEM FUNCTIONS

Based on the projected battery characteristics described above, functional requirements for a battery control system can be defined. Four basic control functions have been identified: Battery Operational Control, Auxiliary System Control, Battery System Status Indication and Fault Detection/Fault Isolation (FD/FI).

BATTERY OPERATIONAL CONTROL

Battery operational control involves monitoring and control of routine battery functions. It can be subdivided into three categories: charge control, discharge control and offline operations.

Charge control is the most critical battery control function in today's battery systems. Ideally, the charge control system returns the battery to full charge following a discharge, equalizes the charge in all cells in a battery and all batteries in a system, and maintains this charge condition until the battery is required to support the loads. To maximize life, the charge control system must perform this function while minimizing stress on the battery. Existing, low voltage Nickel-Cadmium and Nickel-Hydrogen charge control systems utilize constant potential or constant current charging to a temperature compensated voltage limit. Temperature compensated voltage control is typically provided through the power conditioning electronics with voltage levels selected via ground command. Cell and battery equalization is accomplished by applying sufficient overcharge to assure all cells and batteries are fully charged. This approach may not be adequate for higher voltage systems or for other battery chemistries under consideration. Cell or module level voltage monitoring may be required on higher voltage Nickel-Cadmium and Nickel-Hydrogen batteries, and cell or module switching may be required on high temperature batteries which have a low tolerance for overcharge. Lithium-Metal Sulfide systems, for example, have been reported to have low overcharge tolerance (ref. 7). References 8 and 9 describe some approaches for individual cell switching. Indications of charge state may be employed such as ampere-hour return, cell pressure, or electrolyte tank levels in the case of the flow battery systems.

Battery discharge control includes cell or module protection from over-discharge (reversal) and load sharing control. Overdischarge protection on existing Nickel-Cadmium batteries is typically not a concern because the operational depth of discharge (DOD) is usually quite shallow and the number of series connected cells is limited to approximately 30. Deeper DOD's required in GEO applications are limited in number and are usually preceded by

a reconditioning sequence that tends to equalize cell performance. Future batteries, however, will be expected to operate at deeper DOD's on a repetitive basis with over 200 cells in series. Active reversal protection, using cell or module monitoring and switching, may be required to prevent damage or unnecessary degradation. Load sharing control to minimize DOD unbalance in multiple battery systems may also be desirable to maximize battery life and/or minimize battery replacement costs as reported in reference 10.

Battery operational control also includes the control of offline battery functions. A prime example of an offline function is battery reconditioning. Nickel-Cadmium battery reconditioning is performed via ground command on most existing spacecraft systems. Additional offline functions that may be desirable on some advanced battery systems include capacity measurement or equalization charging.

AUXILIARY SYSTEM CONTROL

At this time two categories of battery auxiliary systems can be identified: Thermal Control and Mechanical/Fluid Control.

Existing battery thermal control is typically a passive design requiring rejection of a few hundred watts maximum. Advanced systems with much more severe thermal requirements may require a more advanced active Thermal Control System (TCS). A 50kW battery system will require rejection of 5-10kW_t. In addition, the high temperature battery systems must operate at temperatures ranging from 350° to 500°C. The freeze and thaw cycles on these batteries may also require active control to prevent damage due to thermal shock. Possible control system functions include thermal fluid flow control and heater control.

The category of mechanical/fluid control is directed specifically toward the flow battery systems such as the Zinc-Bromine. This type of battery system presents unique battery control problems since the electrolyte is stored in tanks and pumped through the electrodes to charge or discharge the system. Control system functions here include overall electrolyte management and flow control.

BATTERY SYSTEM STATUS

Battery system status indication consists of both raw and processed data which depicts the current operational status of the battery system. The battery status would be available to the Electrical Power System (EPS) processor or the spacecraft computer for use in on-board power management tasks and transmission to ground stations for engineering evaluation and analysis. At a minimum the battery system status indication would consist of battery system state-of-charge, system configuration, and engineering data.

Battery system state-of-charge would be continuously calculated as a function of variables such as integrated ampere-hours, cell or module voltages, cell pressures, electrolyte tank levels, etc. The system configuration data would include information such as number of operational batteries and cell or module switching configuration. The engineering data would include both raw and processed data such as voltages, currents, pressures, temperatures, and flow rates.

FAULT DETECTION/FAULT ISOLATION

The FD/FI function would continuously monitor the battery system for failure conditions and, when detected, take corrective action to isolate the failure. Where possible, the battery would be reconfigured to minimize the impact of the failure. FD/FI could be used to detect and bypass cell or module open circuits, detect and isolate battery open circuits or shorts, isolate a battery from a charging system failure, protect a battery from thermal control system malfunctions, and prevent electrolyte tank rupture due to overpressure. The FD/FI function can also be extended to switch in redundant equipment if available.

BATTERY CONTROL SYSTEM IMPLEMENTATION

The battery control system functions discussed above can be implemented in a variety of ways. The functions could be handled by the spacecraft computer, the EPS computer or by a specialized battery control unit. A battery control unit can even use local processors at the battery or module level to perform some data acquisition and control functions. A detailed discussion of the conceptual definition of some of these automated power system management techniques can be found in references 11 and 12.

One conceptual battery control system implementation is illustrated in figure 3. The figure shows a simplified solar array-battery power system block diagram. This approach uses a battery control unit which interfaces with the EPS or spacecraft computer. Data from the battery system is acquired by the Battery Control Unit either directly or via local battery or module processors. A list of typical battery system data is shown in table 1. The raw data is conditioned and processed as required. This information, together with the command input from the spacecraft or power system computer, is used to execute the operational control, auxiliary control, and FD/FI algorithms. These algorithms, in turn, generate commands which are transmitted to the Battery System and the Power Conditioning and Distribution Electronics. Typical commands to the battery system can include:

- . Cell or Module Switching
- . Battery Switching
- . TCS Flow Control
- . Electrolyte Flow Control

Commands issued from the Battery Control Unit to the Power Conditioning and Distribution Electronics can include charge voltage and charge current commands. The Battery Control Unit can also generate the battery status information and transmit it to the spacecraft or EPS computer.

CONCLUDING REMARKS

The control techniques developed for low voltage Nickel-Cadmium and Nickel-Hydrogen batteries will not be adequate for the high voltage, high power systems required in the post 1985 time period. Additional active battery control functions other than charge control must be considered for these systems. The additional functions which have been suggested include battery discharge control, control of offline operations, auxiliary system control, battery status monitoring and Fault Detection/Fault Isolation. Existing charge control techniques will require modification. In some cases, totally new approaches will be required to accommodate the new chemistries and high voltage characteristics of these future batteries.

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TABLE I. - TYPICAL BATTERY SYSTEM DATA

<u>Battery Level</u>
Voltage
Current
<u>Cell/Module Level</u>
Voltage
Current
Temperature
Pressure
<u>Auxiliary System Level</u>
TCS Temperatures
TCS Pressures
TCS Flow Rates
Electrolyte Flow Rates
Electrolyte Tank Pressures
Electrolyte Tank Levels

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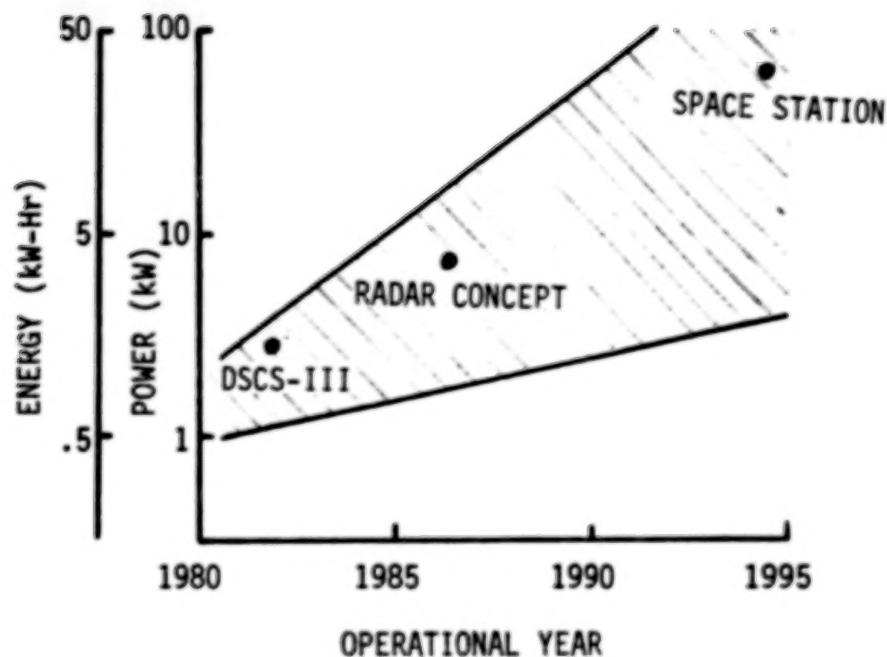


FIGURE 1. - PROJECTED POWER AND ENERGY REQUIREMENTS

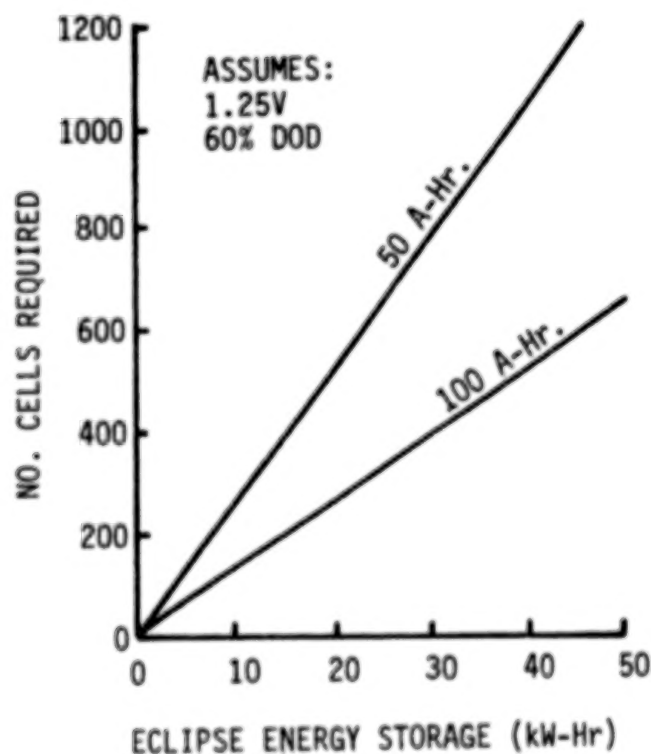


FIGURE 2. - CELLS REQUIRED FOR FUTURE BATTERY SYSTEMS

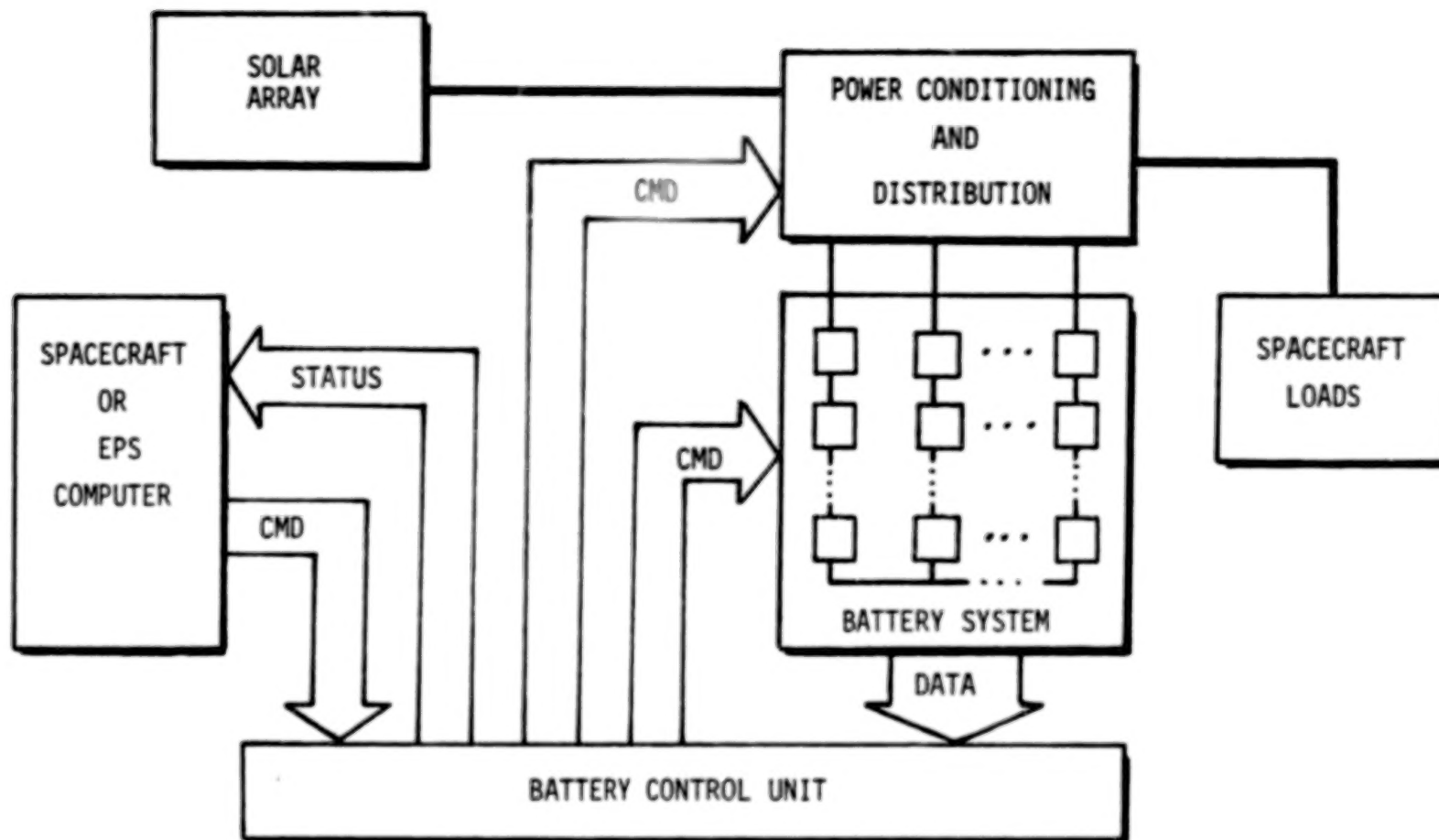


FIGURE 3. - POWER SYSTEM BLOCK DIAGRAM

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279

SESSION III

DISCUSSION

Opening Remarks:

Panel Discussion

Gerry Halpert, NASA GSFC:

"Comparison for Charge Control for Fixed Array vs. Sun Array Intermission"

Q. Gross, Boeing: Which method of charge control provides the most reliable preparation for near-earth synchronous missions?

A. Halpert, GSFC: Fixed array was the S and M and Landsat D mission that I showed examples of in the beginning that were already flying, and having success with that is charging it to the voltage levels, and then without having any ampere hour over in the radar onboard, I showed you the examples of those where we've had very good success and how the fixed oriented ray with the earth satellite where we had to, in order to avoid overcharging for long periods of time and to avoid the heating associated with that and to accommodate that kind of pattern we had to use an ampere hour integrater in addition to the charge/discharge rate to control charge. The difference in this particular case is that you need to have an ampere hour integrater if you will.

A. Aerospace Corporation Representative: Gerry, how did you determine the upper and lower bonds of the charge/discharge ratio curve you showed in Figure #3?

A. Halpert, GSFC: The ratio is always controlled in our case by the hottest battery. As a matter of fact, we had occasion where we had to change the voltage not once but, we had to change the voltage five times. We changed it from level five to level four and ran the level for several months and felt we might be running low so we raised it back to level five again. Then we thought we were overcharging five so we ran it back to level four and reduced to four again. What you have to start with is a good solid system and a good cell and battery system.

Q. Sullivan, APL: Did you consider any reconditioning of the cell? Did you plan on doing that at all?

A. Halpert, GSFC: No, but we probably will take one shuttle off the line to discharge the others a little further than we have before to see what's going to happen if we go to data discharge. Personally I don't think it's been done and I don't think we are going to be the first to try.

A. Arthur, Defense Research: In trying to keep as low acidity ratio as possible, what we found in charge efficiency is the higher the charge rate up to cover three and cover two the lower the C ratio you have to put in. If you charge to a very low rate you have to put in about 60%; if you charge at a very high rate you get away with about 41%.

A. Halpert, GSFC: Our experience with that is we try and get the maximum amount of current as you pointed out in the undercharge region. At the region in the beginning of the charge period the S and M spacecraft is running at the C rate. We put in 24 amps the moment it came into the sun, and so we got in at the C rate. Landsat said these C rates are coming in at about C over X and all of our other satellites that we have been involved with are trying to maintain a cover two. Some of our contractors tend to have lower charge rates, lower solar rate current available and on those kinds of cases we have to be even more careful. But even then we've been quite satisfied with the entire semi automotive spacecraft.

Thierfelder, General Electric:

"Temperature Compensated Voltage Limit:

Jim Masson, Martin-Marietta:

"Advanced Battery Charge and Control for Future Battery Systems"

Q. Sullivan, APL: Do you have any difficulty after some time in orbit where you wish you could raise the voltage limit to higher level in order to charge the battery?

A. Thierfelder, General Electric: We expect to raise the voltage limit on all the batteries especially the ten year missions. In our life test we have raised it after about four years. We normally operate at limit number two, but we expect to charge to limit number three in four and five years and expect to finish each at limit number three.

Q. Scott, TRW: You said that for your synchronous orbit application you picked the actual version from the typical light curves. Did you do the same thing for your lower orbit design and if so what recharge ratio did that give you when you actually put in on test?

A. Thierfelder, General Electric: Well, on the actual test data for the near-earth we had about a 10% charge/discharge ration with the 105 minute orbit. So actually the criteria that Gerry said about a 101 to 110 B, about the same range that we operate in now, of course you would calculate the C to D ratio all the way. Out to the 24 hour period you'll come up with about 130%, probably, but if you stop counting where it levels off they will all be down at 110% or lower.

Q. Scott, TRW: I believe that the current in the battery is sensitive

to voltage in the overcharge or topical light region. Do you not have any trouble with the current drifting because of the tolerance or the drifting of the voltage limit?

A. Thierfelder, General Electric: On our most recent spacecraft one battery is charging at 2/10 of an amp, the other at 4/10 of an amp, and we feel there's no problem when you're down in that low of a range. Someone will say, "Well one is twice as high as the other", that's true but when you're in that low of a current range, when you're down below a cover 100 charge current and one's at a cover 100.

Q. Scott, TRW: Could you comment on the improvement in cadmium - electrode performance that you say you saw.

A. Thierfelder, General Electric: I can't but my co-author sure can.

A. Unidentified, General Electric Representative: Well one thing that Chip mentioned is that we seemed to have retained pretty good cadmium-electrode utilization. I guess the only thing that we can see in the electrode itself that really explains that is that the cadmium-electrode material retains a very high surface area. You see a little bit of growth in overall crystal size from the beginning of life condition to say, seven seasons on life test. But the crystals have a very strongly layered structure, and they appear to be at very high surface areas. We're not totally convinced that this is due exclusively to sequence charging, but certainly this is found in cells that have been sequence charged for about three and one-half years. Furthermore, if you do a little bit of thinking about how active material moves around in the cabin electrode with a little bit of gentle hand-waving, you can convince yourself that sequence charging should have some effect on improving crystal size keeping in low and keeping in high surface area condition in the cadmium-electrode.

Q. Unidentified: Do you have any control? Do any similar cells run along side with other charge?

A. Thierfelder, General Electric: That's the problem. We are always trying to compare tests with about twenty different parameters and you've got to look at a lot of things. I think one thing that showed very clearly how confused things can get is that you put up the curves, to go all over the place and in the real orbit spacecraft operation, nobody runs at the constant depth of discharge for the whole life of the spacecraft at the same temperature.

There are different cell designs, and an awful lot of variables. And if you look at it very closely you can try to eliminate the cell design to some extent and extrapolate to what things would

look like when you compare them on an equal basis. And if you do that you'll find a very small difference between sequence charging and continuous charging. If you look at the cell with more control-like tests, things seem to be even more equal. There may be a slight edge for sequence charging as far as discharge performance is concerned.

- Q. Hafen, Lockheed: I just want to become clarified on what was actually happening in this sequence battery charging. Do the batteries take turns being connected to the solar ray? Is that how it works?
- A. Thierfelder, General Electric: I probably should have deferred sequence charging in the beginning. We define sequence charging ... for instance, in a two battery system one battery would be uncharged, say at the full rate for five minutes. During this five minutes of uncharged period the other battery would be off charged on an open circuit at the end of five minute period. Then the second battery would go on charge full rate, and the first battery would then be on circuit. That's how it continues.
- Q. Thierfelder, General Electric: I just wanted to comment that in the near-earth programs, we also do sequential charging, but slightly different from you. The reason for it is to pick up the efficiency by using higher charge rate. We are kind of marginal in the arrays, so , battery one will take its full maximum current before battery two will turn on and then it will come up to its maximum current, and then battery three will turn on that way. To get the most out of your solar array you do not turn them off and on sequentially, but when they came in, battery three would not charge until there is enough current available first to give two amps to the other two batteries. So are you charging the first battery fully?
- A. Thierfelder, General Electric: No. Say there are only four amps available and the maximum charge is two amps per battery, which is six, so there are only three amps available. I would charge battery one at two amp, battery two at one amp, battery three at no amp. They come up to their voltage limit, so that when battery one comes up to voltage limit it goes into tapering. Next they will sequentially charge So it's a sequential system but somewhat different than yours.
- Q. Zimmerman, Aerospace: I was wondering how you determine the relative effects of this on the nickel and the cadmium-electrodes. Is this based on electro-chemical performance or constructive physical analysis? How is that done?
- A. Thierfelder, General Electric: Most of the results we have at that point are based on constructive analysis on the L-Sat 5 program.

and whatever data might have been available in the literature from other people's constructive analysis.

- Q. Zimmerman, Aerospace: Is the five to ten minute open circuit period an optimum type period, or is it one that is often found to work well in the past?
- A. Thierfelder, General Electric: We haven't really studied the effects of the three minute to five minute, nor have we determined what the optimum might be. That seemed to be a period which would put a considerable amount of charge in the battery and on the other hand the other battery would seek to discharge a considerable amount in the next four minutes. I'd like to hear from people who have had some experiences with charge control systems that have not been entirely favorable in order to let other people know some of the problems and pitfalls to be aware of in using charge control systems. Will Scott has volunteered to be the first.
- Q. Scott, TRW: I don't know how I got myself into this but I can recount one situation which occurred not really by design but just turned out that way, where the original design called for causing the battery to switch between triple charge as a resistor and direct connection to the power bus alternately depending on, in this case, the battery temperature. That is, when the temperature rose to a certain point the battery would switch off the bus to the resistor when the temperature fell down to a certain other point it would switch back-up on to the bus.

This scheme was originally designed about 12 years ago where it wasn't really known very well what the effect of continuous trickle charging at fairly low rates was going to be in a synchronous application. It was felt that the alternating between triple charging and higher rate charging would be a good way to maximize the battery state of charge. I guess there was some data around which indicated that there was some kind of degraded voltage performance to be expected after long periods of trickle charge and this was hoped to counteract this. At any rate, that method worked well with manufactured cells but got us into trouble with another manufactured cell. The basic cause of the trouble with the second manufactured cell was that after a couple of years of cycling the characteristics of the battery changed to the point that when the battery switched from trickle charge back on directly to the bus it would receive quite a high current, and at this period of time the battery would stay on the bus and could be of the order of an hour or two, or even longer depending on how long it took the temperature to come back up again. So it wasn't anything like the alternate charging that was just discussed on the last paper. What ultimately happened was apparently the cells were overstressed because of the peak

charging current which did take off after awhile. But while it was high we believe it caused overheating and excessive pressure on the cell after a period of time, and caused certain cells to become partially oriented. We confirmed this pretty much by tests on the ground and the reason that we use this system in the first place instead of using temperature to switch was because we had three batteries located at different points on the spacecraft and we could not keep the same temperature, so we allowed each to switch independently, based on its own temperature.

COMMENT

Baer, GSFC: I just have a general comment. I think most charging systems work quite adequately when everything goes as planned, but we may lose a lot of flexibility in the system because when the unplanned problems happen, or the depth discharge increases, that's usually when you start getting into trouble. Therefore, I think the system needs a lot of flexibility.

COMMENT

- Q. Halpert, GSFC: One of the reasons we got into charge and discharge sequence is that our first mission died on us, not because of sequential charging but because the electronics that happened to fail, and we got stuck on the number one battery, with the highest charge rate, and that rate didn't get it off. I'm not too sure whether sequential charging would be desirable in a new earth orbit. Maybe somebody else can make a comment.
- Q. Gross, Boeing: I believe, Gerry, that your sequential charging method was limited, intended primarily for geosynchronous orbit. Is that correct?
- A. Stockel, Comsat: Sid, this is in reference to the nickel-hydrogen battery. On the MGS2 the charge control is temperature. What I mean by that is it switches from the high rate charge to the low rate charge so when the temperature reaches a pre-determined value and that value is commendable from the ground. It worked fine when the spacecraft was operating with all its designed load; however, after a few years of that operation with one of the main loads of the spacecraft filled what happened was the battery started charging, the temperature was much, much lower than it was when the payloads were on. Consequently it took a longer time to reach our lowest temperature set and as a result we had excessive overcharge.

COMMENT

Halpert, GSFC: Do you want to support the first comment about the fact that you need a charging system such that if you do have a failure with one of the cells, one of the batteries, that the charge system can contain it? And that gets back to a comment that Sam had asked earlier about what happens to the cell when it fails in one of the three batteries. We did republish a report a couple of years ago in which we purposely shorted out one cell in a 22 cell battery and ran it in parallel verses another 22 cell battery. That is, 22 cells and 21 cell were connected together and we ran them through several thousand orbits and the same VT type charge with the taper current. It was true we were overcharging the bad battery, the U cell battery, considerably, maybe a size 20% every time. And the battery with the 22 cells only had 90 - 95% maybe 97% of what we took out - but even then we still were able to use several thousand cycles. And when we discharged it down at the end we got almost the same capacity as when we started. So we don't understand why we were able to put 99-98-97 percent back in and still get full capacity. The point I'm trying to make is here we have a direct shortage cell on the one leg and we are still able to contain and operate for an extended period of time without a catastrophic failure.

M.C.: On the next subject is there anyone who would like to make any comments regarding a truck control system they have used which they have found to be very satisfactory and which has not been discussed this morning? I should point out that there are other charge control systems that have been used a lot and we were hoping to get another paper on the two-step charge system.

- Q. Unidentified: I guess this applies to both Helm and Gerry. That is, how many charge control steps do you both feel are necessary for the normal charge and for the trickle charge? I'll leave the trickle charge out of it, how many steps in this do you see desirable?
- A. Halpert, GSFC: Since I have the microphone, first of all I want to add something to what I've previously said. In addition to the temperature voltage limit we also have the maximum charge two levels, the high which I showed and we have the low which is sort of a contingent type current control and the lower level is only by design to be used when we come out of reconditioning. Rather than go to the maximum current levels, which I have shown, we go to a lower current level and also the lower current level is envisioned to be used in case the entire temperature voltage limit should fail then we would switch to the lower current level which is like a C over 30 rate. So from what Dave said we probably have a

lot more flexibility in the system than I have brought out so far. In addition to what I've shown we also have the two charge levels. In answer to the question asked, you'll notice that, NASA has eight levels and we have four. Many people have asked why we don't have eight but we have considered at several times using eight levels; but in the case of Gerry he showed that they have made use of all eight. We have determined without custom designing of the levels that we cut a low level one which is only a contingency type level which we have used in some cases to reduce temperatures if they were high. I guess on one program they went to a level one and we have a level three so that in a cells age we can go to a level three. Level four is a contingency level but we traded off four levels and eight levels. There's not too much complexity in going to eight, there is only one more command; but we'd have four more group commands. The thing that decided for us was that the people who operate our spacecraft have considerable questions about how to use which voltage level and when, and we have written many instructions, and so after going round and round on the operational phase of it we decided if we had eight levels this problem would increase two fold, thus causing the operational people to be, in many cases overreactive and wanting to make changes. Actually our system is designed to be automatic and unless something very serious happens you do not have to command anything into the power system. The power system will run hopefully through the whole mission without requiring any commands at all and I've been in operational control on a number of our systems and the operational people, ah, well we try to keep it as simple as possible. The main reason not having eight is we feel that we don't need them, and they just make the operation more complex.

Well, we do have eight because we would design it for a specific mission but it is part of the modular power subsystem, which is a component on the multi-mission modular spacecraft and that gives us the range that we're looking for. We wanted to build a power system capable of operating under a number of different kinds of conditions. I told you about two this morning, the fixed array, and the seen oriented array, possibly for synchronous mission or whatever. So we want to give it a lot of flexibility. Although I think level seven is not even charged, two or three are more for a case in which we would have one cell fail in one of the batteries so we could operate at a lower level. The upper level eight we actually used in a test we had a four pack test of a standard cell program which we operated 40% depth of discharge at 30°C, 40% depth of discharge at 20°C, 40% and 10°C and then the last one was 25% depth of discharge at 20°C. In operating the 30°C, 40% depth of discharge at 20°C. In operating the 30°C pack we obviously started degrading rather rapidly and the capacitor started to leave us on the bottom end and the only chance we had in terms of what we would do on a mission if we had that problem is raise the voltage level. We started at level seven and went down to level six. Then the degrator went back up to level seven and finally to level eight before we turned it off and that was a period of a year and 1/2. So we operated 40% depth of discharge 30°C for one and 1/2 years. In our missions we would never expect to use, unless

unless under extreme conditions, the eighth level. So we have the eighth level for flexibility.

- Q. Betz, NRL: Gerry, on the ampere hour integrade you're going to be using on this new mission, how many selectable recharge fractions do you have available in that system?
- A. Halpert, GSFC: In that particular case, Fred, all we are going to change is the voltage level, and when the C and D ratio has been reached we are going to break down to trickle charge. I think there is one current for trickle charge, there may be two, but I think it's only one.
- Q. Betz, NRL: Gerry, what C and D ratio is the ampere hour integrator set for?
- A. Halpert, GSFC: There was a curve I showed this morning, I'd be happy to give you a copy of it, that had four levels of charge and discharge ratio that one could select to change the current into the trickle charge mode. We picked up the second level on the chart, if you could go back and see that, it seemed to work adequately.
- Q. Aerospace Representative: Getting back to the question that Gerry answered a few minutes ago I would think that, particularly in batteries running at high DOD's and high voltages, it might be possible or desirable to have redundant cells in the batteries in the event of failures of what ever kind. Could I ask the speakers to comment on this?
- A. Thierfelder, General Electric: Well, one comment on what I presented so far, is existing spacecraft. We are looking at big power systems. We do envision the same things that Jim Masson reported on. One of the things in common with others is we feel like there will be a lot of switching of cells in and switching of cells out, and modules in and modules out. They are big systems of hundreds of cells and series paralleling these batteries, each having a hundred cells. There's going to be a lot of switching going on. We have studied the large systems also.
- Q. Aerospace Representative: What about in your present systems? In the event of a self-short how do you maintain voltage that is required? Gerry mentioned that.
- A. Thierfelder, General Electric: Well, the question was asked before what we would do. The system is designed for a redundant battery so if there is a failure in a battery we can switch that battery out and operate on the other two for the mission; however, it may not be necessary to switch out the battery. If it's just partially short

itself it could still share the load. The question then comes up if the inefficiency of that battery would cause a problem with the solar ray not being able to furnish enough power, because that would be operating inefficiently and it would take a lot of current on charge and very little power on discharge. There would be nothing catastrophic if the cell failed in one of the batteries. The general instructions are to switch that battery off the line and it would then depend from there what we would do in that battery.

- Q. Ford, Aerospace: Question for Gerry. On the mission where you are flying ampere hour integration, did you consider just doing away with the VT limits at all? All together could you fly with only the integrator? Do you know if decisions were made on that? On whether we considered using any other than MPS type data?
- A. Halpert, GSFC: Okay. Well we had planned on using modular power systems type charge control and so we did not look at any other type for this purpose. We tried to, knowing what our concern was for the, ah, really to have enough current to charge, we tried to work within the system, and that was the only way we could make the adjustment. Although on that system they are not using the modular powered subsystem.
- Q. Ford, Aerospace: Do you have the ability to bypass the VT limits?
- A. Halpert, GSFC: We have the ability to go trickle charge or switch the battery off one independently. We cannot switch all three off, only two, but we can't do without the cell. If we wanted to trickle charge yes we would be able to trickle charge continually but obviously that one's not going to get us charged in 90 minutes or in 60 minutes.
- Q. Joe Stockle, ComSat Labs: I'd like to ask the panel a question. Do you think these charge control schemes are applicable to nickel-hydrogen as well as nickel-cadmium systems. With the nickel-hydrogen of course you have added dimension of pressure as a indicator as a state of charge.
- A. Betz, NRL: I guess I'll start with that one but I also wanted to answer some more of the question that Al asked from Aerospace, and that is about the switching of cells in and out of the circuit. One of the considerations in a high voltage battery is not only the number of cells in a series but what kind of cell you are dealing with. Chuck Willard from TRW mentioned what they had done at least with reliability analysis, through high voltage battery, and the results showed from the mathematical standpoint that the battery, the reliability, didn't appear to be a big swinger. One of the things depends on what kind of a failure mode you are looking for. If you assume in nickel-cadmium system that

an open circuit self failure is not a realistic thing then I guess I've seen some information somewhere that said that no one has ever really reported seeing an open circuit nickel-cadmium failure. Maybe if you just assume the short mode you may not have to switch cells out. Nickel-hydrogen, on the other hand, I know there is a lot of concern about an open circuit failure in that kind of a system, in which case, now the switching of the cells, maybe not for charge control but at least from a fault detection standpoint, may be desirable or may be even required to preclude you from having a total battery failure from the individual cells.

SESSION IV

"RECONDITIONING HAS SIGNIFICANT EFFECT ON
BATTERY LIFE: FACT OR FICTION?"

David F. Pickett, Jr.
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RECONDITIONING HAS SIGNIFICANT EFFECT ON

BATTERY LIFE: FACT OR FICTION?

David F. Pickett, Jr.
Hughes Aircraft Co.
Space and Communications Group

ABSTRACT

Battery reconditioning regimes are used as a matter of routine by practically all spacecraft users in order to partially recover voltage lost as part of the battery ageing process. Reconditioning techniques vary with respect to final end of discharge voltage and method of applying the reconditioning load. There are certain cost benefits claimed for reconditioning. Theory on battery voltage decay requiring reconditioning is not well established. Prior to emergence of Ni-H₂ batteries the cadmium electrode was believed largely responsible, but recent data shows that the positive electrode also contributes to some extent. It appears that reconditioning is required to sustain voltage levels near those at beginning of life, but uncertainty exists as to its effect if lower voltages can be tolerated.

INTRODUCTION

Battery voltage always decays as a function of time in-orbit and will eventually reach an inoperable value in the absence of power conditioning or reduction of spacecraft eclipse loads. A temporary partial recovery of voltage can be effected by discharge of the battery to a low voltage level (~ 1.0 volt/cell) followed by recharge at a rate greater than C/20 with overcharge of 10% to 30%. The discharge is usually carried out at the C/50 rate or lower through a fixed resistance. Higher discharge rates (C/2 - C/4) to a low voltage followed by lower rates (C/50 - C/100) to 1.0 volt/cell or lower have also been claimed to be effective. This discharge at low rates to very low voltage levels followed by recharge for purposes of partial recovery of battery voltage and capacity is referred to as reconditioning.

Reconditioning is most always performed on batteries in Geosynchronous Equatorial Orbit (GEO) or in 12 hour orbits just prior to each eclipse season. Data on reconditioning in Low Earth Orbit (LEO) is limited, but can be effective and feasible under certain conditions.

PANEL DISCUSSION

In order to address the questions concerning possible battery life increase associated with reconditioning four panel speakers will discuss certain aspects of reconditioning during this session. Questions will be entertained after each speaker's presentation.

Discharge below the 1.0 volt/cell level to a value of about 1.0 volt/battery has been advocated by the people at TRW as being a more effective way of reconditioning batteries and claimed to be the key to successful deep depth of discharge operation in GEO. This type of reconditioning is called Deep Discharge Reconditioning. It will be discussed by Dr. Willard R. Scott in his presentation, "Deep Discharge Reconditioning Pros and Cons".

The safest way to recondition a battery below the 1.0 volt/cell level is to have individual resistors or shorting relays across each cell so that its reconditioning discharge is independent of the other cells at low discharge voltages. A technique of this type is described by Steve Gaston of RCA Astroelectronics in his presentation, "Unique Battery Reconditioning Cycle for RCA's Geostationary Satellite".

The Ford Aerospace view on reconditioning will be given by Gert van Ommering and is titled "Costs and Benefits of In-Orbit Reconditioning".

Probably the most recent controversial aspect of reconditioning will be addressed by Dr. Chuck Badcock of the Aerospace Corporation. He will address the effect of reconditioning on the positive electrode.

DEEP DISCHARGE RECONDITIONING - PROS AND CONS

W. R. Scott

TRW Space and Technology Group

INTRODUCTION

Despite the increasing use of reconditioning intended to increase and/or prolong the usefulness of alkaline batteries in orbiting spacecraft, considerable misunderstanding and controversy persist about the practice. This confusion is due for the most part to the large number of different possible ways that reconditioning may be carried out, the associated variety of results that have been obtained, and the lack of information from controlled tests to provide guidelines and allow predictions to be made. While this paper does not provide the latter, it does attempt to organize some of the "art" of reconditioning and to present a balanced picture that will hopefully assist users in applying this concept.

WHAT IS RECONDITIONING

It is useful to distinguish between a reconditioning procedure and a reconditioning effect. These may be quite independent, as it is possible to carry out a reconditioning procedure, i.e., perform "reconditioning," and yet produce little or no reconditioning effect (such as increased discharge voltage and/or capacity). The procedure comprises the operations and sequence carried out on the battery that are designed to produce the desired effect. These are discussed below. Whether there is a significant effect on battery performance depends on the specifics of the procedure used and on the nature of the problem with the battery. This dependence of the "cure" on the underlying cause of performance degradation is not widely recognized. Inattention to this relationship can result in unsatisfactory results.

The reconditioning effect is more difficult to define, as it differs from case to case depending on the usage being made of the battery, the condition of the battery, and the reconditioning procedure used. Generally, discharge voltage is increased and hence watt-hour capacity is increased whether or not there is an increase in ampere-hour capacity. With the appropriate procedure it is usually possible to increase both watt-hour and ampere-hour capacity significantly for some number of cycles. Charge voltage is also increased to a level near that of a newer cell. Furthermore, there is some evidence that charge efficiency and charge acceptance are increased. On the other hand, reconditioning will not revive a cell with a hard short. However, appropriate reconditioning has materially increased the useful capacity of partially shorted cells,

thus allowing batteries containing such cells to continue to support a load long after they would otherwise have been turned off.

CAUSES AND CURES

The simplest procedure that has been found to have a reconditioning effect is open circuit stand. The effect is usually observed during ground tests under low-earth orbit conditions when testing is interrupted by unplanned events. The degree and longevity of the improvement observed is small compared to that from other procedures. The cause of the degradation that responds to open circuit stand is not known; one may speculate that it is probably electrolyte redistribution.

Another reconditioning procedure used is prolonged overcharging, i.e., extending overcharge well beyond that achieved during routine cycling. This can be effective in low-earth orbit (LEO) where recharge time is limited during normal operation, but appears to be of little value in geosynchronous orbit (GEO) where many hours are available for recharging during eclipse seasons. This difference exists because reconditioning by overcharge can only be effective when the cause of the performance degradation is inadequate recharge during routine cycling, thus allowing the cells to "run down" to some extent. Appropriate trickle-charging in geosynchronous orbit usually prevents such run-down. If inadequate charging is allowed to continue too long without a change in the routine, a semi-permanent or permanent loss of some charge acceptance may occur because of the inactivity of the uncharged negative material. This condition is difficult to reverse under spacecraft operating conditions and hence should be prevented. After the condition has developed, prolonged low-rate overcharging sometimes has a reconditioning effect.

Evidently a commonly occurring cause of voltage and/or capacity decline with cycling (often referred to as "fading") in nickel-cadmium cells, is the gradual accumulation of difficultly dischargeable charged active material in the electrodes, either positive or negative or both. This form of fading occurs because the cells are operated from the fully charged condition down, and as a result the charged material that is rarely if even discharged atrophies. Electrolyte redistribution may also accompany this process, resulting in insufficient electrolyte in the areas where it is needed for discharge.

The remedy for this condition is to exercise all or as much of the accumulated inactive charged material as possible, preferably at regular intervals. To do this the inactive material must somehow be completely discharged and completely recharged. Such complete cycling tends to restore the electrodes to an active condition and also serves to restore proper electrolyte distribution.

The discharge difficulty referred to shows itself as a relatively low cell voltage at higher depths of discharge at normal load current. Unlike the case of a new cell, the voltage of a heavily cycled cell is

highly sensitive to discharge rate at depths of discharge greater than used during normal cycling. The degree of this sensitivity increases as the number of cycles to any limited depth of discharge increases. However, by decreasing the discharge current sufficiently, practically complete discharge can be obtained at an acceptable cell voltage. The point to be made here is that the effectiveness of the procedure depends on the depth of discharge attained, not on the cell voltage reached. The cell voltage at any depth of discharge will depend on the condition of the cell and the discharge rate used. Thus the term "deep discharge reconditioning" (DDR) should be interpreted to refer to the depth of discharge involved, not to the voltage levels observed. The more frequently this form of reconditioning is performed, the higher the cell voltages remain during the process.

One result of regular and repeated DDR observed in GEO missions is that the capacity of the battery increases with time. This increase, although apparently advantageous in that it decreases the effective depth of discharge, can have an undesirable effect if it becomes too large. If, as is likely, the capacity growth occurs by an increase in the utilization and maximum state of charge of the positive electrode, the growth occurs at the expense of an equal amount of overcharge protection on the negative electrode. Since some minimum of overcharge protection must be preserved, the amount of capacity growth must be controlled. This may be done by varying the frequency of DDR based on the capacity measured during each deep discharge.

The use of very low rates (often in the range from C/200 to C/1000) for deep discharging also has potential disadvantages. The length of time that each battery must be off line for DDR-usually four to seven days including time for recharge- is not normally available in LEO when there is no battery redundancy and when continuous cycling cannot be interrupted. Reconditioning in LEO can be facilitated by use of multiple batteries operated in parallel so that only a small charge in the on-line capacity results when one battery is disconnected.

The time required for DDR is becoming an increasing problem for military communication satellite operations in GEO where dedicated ground station attention is required, as ground station time per satellite is decreasing rapidly. Thus automatic, on-board control of reconditioning will become necessary in the near future.

The time required for DDR may be minimized by using more than one rate for discharging. The battery may be discharged to its normal, in-cycle depth of discharge at the load rate, then the current may be decreased for the remainder of the discharge. This type of current profile is obtained automatically when cells are discharged on individual fixed resistors. The effectiveness of this procedure compared to that of discharging all the way down from the fully-charged state at a low rate is not known quantitatively, but the difference, if any, is expected to be small.

Another potential disadvantage to low-rate discharging of nickel-cadmium cells is a possible degrading effect on the cadmium material (Ref. 1). It has been shown that repeated low rate discharges result in the growth of large crystals of $\text{Cd}(\text{OH})_2$ and eventually result in negative - limiting on charge and a loss of charge acceptance. However, results of the use of DDR to date show no evidence of any loss of charge acceptance, at least in GEO. Apparently the beneficial effect of DDR on the cadmium electrode exceeds any detrimental effect of low rate discharging for the number and frequency of discharges performed in GEO (usually two to four per year at three to six month intervals).

DDR PROCEDURES

Procedures used today for performing DDR vary widely, differing in the discharge rate, the criteria for ending discharge, and whether the discharge load is applied to individual cells or to batteries with many cells in series. The significance of discharge rate in degraded cells, especially at high depths of discharge, was discussed above. It was pointed out that cell voltage is an unreliable criteria to use for ending the discharge, as voltage in a cycled cell at points short of complete exhaustion of real capacity is highly sensitive to cell condition and discharge rate. However, when batteries are discharged at the battery terminals, cell voltage becomes a cut-off criteria if no cell is to be allowed to reverse regardless of what depth of discharge is attained. Unfortunately few if any spacecraft in the past have had the capability of telemetering cell voltages to the ground or even of acquiring cell voltage data on board for use in automatic control of discharge current. With only battery terminal voltage to work with, operators on the ground must guess at the correlation between cell voltages and battery voltage. When no cell reversals are allowed, the tendency is to cut off discharge at a relatively high voltage, usually ≥ 1 volt per cell, with the result that a lot of capacity may remain undischarged, and the effectiveness of the discharge thus may be less than optimum. Many future spacecraft will have on-board battery voltage acquisition and processing so that interpretation of battery voltage during DDR will not be necessary.

As long as the battery voltage, and by inference the cell voltages, remain in the range considered safe, another criteria may be used for cut-off that may result in the saving of time or in a higher than minimum end-of-discharge voltage, namely, ampere-hours (A-h) discharged. It is reasonable that the total A-h discharged during DDR should increase as the normal load DOD increases, although this relationship has not been demonstrated by test. For example, experience at TRW (Ref. 2) has shown that, for a normal maximum DOD of 70 percent in GEO, if just that number of A-h equal to the actual new-cell capacity to 1 volt per cell at the C/2 rate is taken out at the $< \text{C}/100$ rate during DDR, the reconditioning effect is excellent and the end-of-discharge voltage remains well above the equivalent of 1 volt per cell. A somewhat lower or higher A-h target should serve as well. However, use of the A-h criterion requires monitoring discharge current and calculation of cumulative A-h on the ground with existing spacecraft. In the future an on-board A-h integrator and control function will handle this chore.

Even when battery voltage is used for cut-off, it is useful to monitor A-h discharged for DDR. If the A-h at cut-off is only a small percentage greater than discharged during load cycling, the effectiveness of that reconditioning cycle will be marginal. When this occurs, and time permits, a second cycle should be performed, whereby better results are usually obtained under a battery voltage constraint.

THE CELL REVERSAL ISSUE

When a battery is deep-discharged at the battery terminals, the voltage of first one and then more cells will go below zero until and unless the discharge is stopped. The poorer the battery condition the sooner the first cell will become reversed. If, therefore, the discharge is stopped before the first cell of a badly degraded battery is reversed, the depth of discharge may not be much greater than that during regular cycling. Thus the use of the first cell reversal (however this might be detected) as a criterion to stop discharging can severely limit the effectiveness of the discharge. If, on the other hand, reversal of cells under these conditions is allowed, a large reconditioning effect may be achieved in one cycle - not because the cells are reversed, but because of the high depth of discharge achieved.

The risk of reversing nickel-cadmium cells during DDR is controversial at this time. While it is well established that repeated reversal at higher (e.g., $\geq C/4$) rates can result in high pressure due to hydrogen gas and to shorting, there is no firm evidence that either high-pressure or shorting is caused by infrequent discharge of cycled cells into reversal at very low rates. However, the region of rates between $C/100$ and $C/10$ is not well characterized in this respect. It has been shown (Ref. 3) that an older cell when reversed at the $C/10$ rate experienced little effect in a short time but after many hours became shorted. However, no cell in a battery would experience prolonged reversal at the $C/10$ rate. In other work (Ref. 4) a battery of cells was tested using DDR involving reversal of some cells at the $C/100$ rate in a simulated GEO mission profile. Although some change in cell impedances toward lower ohmic values was measured during reversal, no shorting occurred and the cells were normal after recharge. These authors suggest that although no shorting occurred in this test, the repeated exposure of the cells to conditions that caused the impedance to decrease (i.e., reversal) might increase the tendency of the cells to develop shorts in the long run. This suggestion is speculative and questionable in view of the fact that six months, an eclipse season of cycling, and four months of trickle charging take place between each reconditioning sequence in a GEO mission.

The uncertainties of cell reversal can be avoided if the cells are discharged individually rather than as a series string (Ref. 5). A fixed resistor across each cell will give a discharge current profile that remains roughly constant until useful cell capacity is near exhaustion, then decreases as the cell voltage decreases. Such a profile is well suited to DDR, and the resistors may be left connected for long periods without harm to the cells. Relay switches, with associated drives, logic, command circuitry, etc., must be provided to connect and disconnect the cell resistors, and the weight and

cost of these components is significant. However, the operational simplicity of this approach may justify the extra cost and weight, especially when customer requirements prohibit reversal of cells under any circumstances.

CONCLUDING REMARKS

Deep-discharge reconditioning (DDR) can be of great benefit to battery performance, especially in geosynchronous orbit, if performed properly and regularly, and can be essential to operation of batteries at the high depths of discharge (DOD) required to minimize weight. The procedure should be tailored to fit the nature of the degradation occurring during regular cycling. DDR is not without its drawbacks, however, and these differ depending on the normal DOD to be sustained and/or whether the discharge is done at the battery or the cell level. Battery-level discharge carries the minimum weight penalty but raises questions of the effects of low-rate cell reversal that as yet have no firm answers. Cell level discharge avoids cell reversal but carries significant penalties of weight and complexity. Thus no universal procedure or method of implementation of deep-discharge reconditioning is now available and thus the various approaches must be evaluated for each application.

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SPACECRAFT BATTERY RECONDITIONING
COST CONSIDERATIONS

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SPACECRAFT BATTERY RECONDITIONING COSTS - MANUFACTURING

<u>NON-RECURRING</u>	<u>RECURRING</u>
DESIGN AND DOCUMENTATION	HARDWARE
MECHANICAL LAYOUT	CONTROL UNIT FABRICATION
THERMAL ANALYSIS	HARNESS FABRICATION
ELECTRICAL LAYOUT (HARNESS)	MECHANICAL INTEGRATION
COMMAND AND TELEMETRY DESIGN	UNIT LEVEL TESTS
PROCEDURE DEVELOPMENT	SYSTEM LEVEL TESTS
ENGINEERING MODEL HARDWARE AND TESTS	PROGRAM OVERHEAD
QUALIFICATION MODEL HARDWARE AND TESTS	
PROGRAM OVERHEAD	
<u>ESTIMATED COST</u>	<u>ESTIMATED COST</u>
\$25 K/PROGRAM	\$4 K/SPACECRAFT

SPACECRAFT BATTERY RECONDITIONING COSTS - OPERATIONS

<u>NON-RECURRING</u>	<u>RECURRING</u>
OPERATIONAL PROCEDURES DEFINITION	PLANNING AND SCHEDULING
CONTROL SOFTWARE DEVELOPMENT	RECONDITIONING MONITORING
OPERATOR TRAINING	DATA REPORTING
OPERATIONS OVERHEAD	DATA EVALUATION
	OPERATIONS OVERHEAD

cont...

ESTIMATED COST

\$5 K/PROGRAM

ESTIMATED COST

\$7 K/SPACECRAFT/RECONDITIONING

SPACECRAFT BATTERY RECONDITIONING - COST SUMMARY

MANUFACTURING

NON-RECURRING* \$25 K/PROGRAM

RECURRING \$ 4 K/SPACECRAFT

OPERATIONS

NON-RECURRING \$ 5 K/PROGRAM

RECURRING** \$ 7 K/PROGRAM

*LOWER COSTS OFTEN POSSIBLE DUE TO TECHNOLOGY CARRY-OVER FROM PREVIOUS PROGRAMS.

**COSTS WILL VARY WITH THE NUMBER OF SPACECRAFT BEING MANAGED BY THE SAME GROUND CONTROL CENTER.

POTENTIAL COSTS OF NOT RECONDITIONING

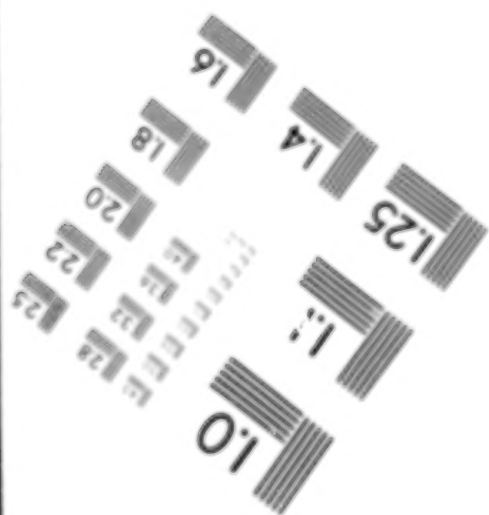
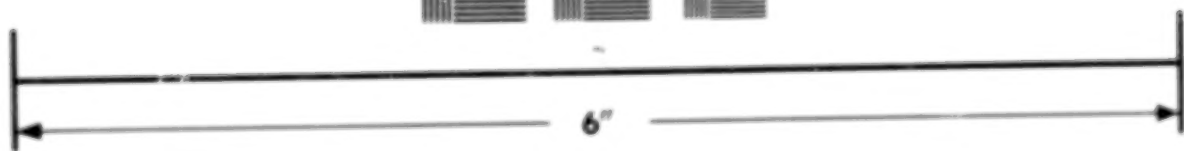
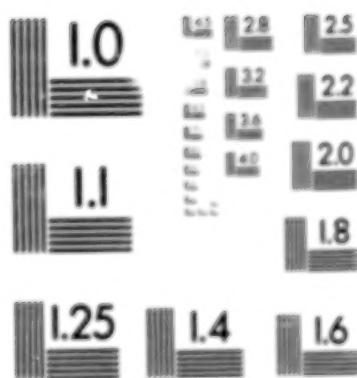
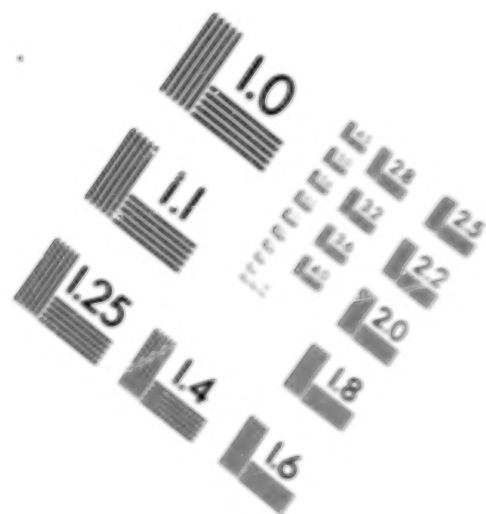
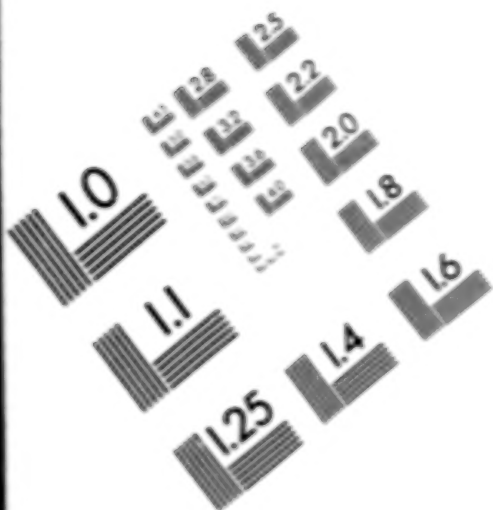
- REDUCTION IN OPERATIONAL LIFE OF THE SPACECRAFT
- LOAD REDUCTIONS IN ECLIPSE LEADING TO REVENUE OR DATA LOSS
- INCREASE IN SPACECRAFT MANAGEMENT LABOR COSTS

SEE FIGURES...

TABLE 1.

RCA ASTRO GEOSTATIONARY SPACECRAFT OPERATING IN ORBIT

<u>SPACECRAFT</u>	<u>LAUNCH DATE</u>	<u>CUSTOMER</u>
o SATCOM F1	December 1975	RCA AMERICOM
o SATCOM F2	March 1976	RCA AMERICOM
o ANIK B	November 1978	TELESAT OF CANADA
o SATCOM III	November 1981	RCA AMERICOM
o SATCOM IV	January 1982	RCA AMERICOM
o SATCOM V	October 27, 1982	RCA AMERICOM



RECONDITIONING COSTS PER SPACECRAFT - K\$ (1982)

LIFE (YEARS)	NUMBER OF SPACECRAFT IN PROGRAM						
	1	2	3	4	6	8	15
1	48	33	28	26	23	22	20
2	62	47	42	40	37	36	34
3	76	61	56	54	51	50	48
5	104	89	84	82	79	78	76
7	132	117	112	110	107	106	104
10	174	159	154	152	149	148	146

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COST PER DAY PER SPACECRAFT* - K\$ (1982)

LIFE (YEARS)	SPACECRAFT INITIAL COST** - M\$ (1982)				
	50	75	100	150	200
1	147	220	293	440	586
2	78	117	156	234	312
3	55	83	111	166	221
5	37	55	74	111	148
7	29	44	58	87	117
10	23	35	47	70	93

*DOES NOT INCLUDE OPERATIONS COSTS

**INCLUDES DEVELOPMENT AND LAUNCH COSTS

LIFETIME RECONDITIONING COSTS EXPRESSED AS
EQUIVALENT OPERATING TIME (DAYS) WITH THE SAME COST
(75 M\$ SPACECRAFT)

LIFE (YEARS)	NUMBER OF SPACECRAFT IN PROGRAM						
	1	2	3	4	6	8	15
1	0.2	0.2	0.1	0.1	0.1	0.1	0.1
2	0.5	0.4	0.4	0.3	0.3	0.3	0.3
3	0.9	0.7	0.7	0.7	0.6	0.6	0.6
5	1.9	1.6	1.5	1.5	1.4	1.4	1.4
7	2.0	2.7	2.5	2.5	2.4	2.4	2.4
10	5.0	4.5	4.4	4.3	4.3	4.2	4.2

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CONCLUSIONS

- COST OF PERFORMING RECONDITIONING IS MINUSCULE COMPARED WITH SPACECRAFT SYSTEM INVESTMENT
- SPACECRAFT LIFE EXTENSION OF A FEW DAYS JUSTIFIES INCORPORATION OF RECONDITIONING CIRCUITRY

UNIQUE BATTERY RECONDITIONING CYCLE FOR RCA's
GEOSTATIONARY SATELLITES AND ITS APPLICABILITY FOR
LOW EARTH SPACECRAFT

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RCA Astro-Electronics

ABSTRACT

Six (6) geostationary spacecraft, manufactured by RCA Astro, are presently operating in orbit. All of their batteries are performing well. They all contain unique battery reconditioning circuitry, permitting individual cell reconditioning to practically zero volts without the danger of cell reversal. This reconditioning is performed just prior to start of each eclipse season. This technique has maintained the battery's end-of-discharge voltage with mission life. The oldest operating RCA Astro geostationary spacecraft, Satcom F1 and F2, have now completed almost 7 and 6-3/4 years in orbit, respectively. Their battery performance, reported herein, show that a major milestone in the mission longevity of nickel-cadmium batteries has been achieved.

Low earth orbit test data show a long lasting effect of maintaining end-of-discharge voltages for nickel cadmium cells using periodic reconditioning. The unique RCA light-weight reconditioning circuitry can accomplish a quick reconditioning and prevent cell reversal. Reconditioning, thus, has the potential for extending mission life of geostationary as well as low earth orbit spacecraft, when two or more batteries are present.

INTRODUCTION

The batteries for all RCA geostationary spacecraft contain unique reconditioning circuitry. Its purpose is to minimize cell end-of-discharge voltage degradation during their missions. This circuitry provides for a full individual cell electrical drain to practically zero volts and prevents the higher capacity cells from pushing the low capacity cells into a reverse potential. In this manner, reconditioning including a full recharge is accomplished in 4 days (96 hours) or less. Thus, reconditioning during the mission is conducted just a few days before the spacecraft enters each eclipse season. This sequence maximizes the effect of reconditioning during the eclipse discharge. The reconditioning circuitry is located on the battery package and is of light-weight design. Two sets of relay contacts are provided for each reconditioning resistor set for redundancy. This assures a reliable draining resistor removal after completion of the electrical drain. Each relay has a minimum operating life of 100,000 cycles and

only 20 cycles are required during a 10 year mission.

BATTERY PERFORMANCE IN ORBIT

RCA Astro has manufactured 6 geostationary spacecraft which are presently operating in orbit using nickel-cadmium batteries. Their nomenclature and launch dates are listed in Table 1. All batteries are performing well. The battery performance of Satcom F1 and F2 is of prime interest since they have been operating the longest in orbit, almost 7 and 6-3/4 years, respectively. Their design and earlier mission performance were reported in 1980 (Reference 1) and at the 1976 through 1981 Goddard Space Flight Center Battery Workshops.

Figure 1 shows the minimum average battery voltage for Satcom F1 and F2 as a function of the number of eclipse seasons in orbit. Satcom F2 had received a forced daily eclipse of approximately 27% depth-of-discharge during the continuous suntime duration until eclipse season number 6. This daily eclipse, in conjunction with a less than full recharge achieved between these eclipses, had resulted in some voltage degradation. This voltage however, recovered when the daily eclipse sequence was discontinued following eclipse season number 6. The batteries of both spacecraft in general show very small, if any, voltage degradations, excluding eclipse season number 1 on F1 and correcting for the different regime applied to F2 during the first 6 seasons as described above.

Figure 2 shows the same data as for Figure 1, except it presents the minimum average cell voltage using an expanded scale and shows the predicted voltage degradation established earlier using Crane data of packs 207A and 209A (Reference 2). It can be noted that the voltage degradation was considerable less than was predicted and cell voltage is substantially above the minimum required for a full payload operation.

Figure 3 shows the maximum average depth-of-discharge (DOD) for the Satcom F1 and F2 batteries as a function of eclipse season. For both F1 and F2 it ranges from 57% to 52% based on the nominal capacity for their first 14 and 12 eclipse seasons, respectively. For F2 on eclipse season 13 the DOD was reduced to 42% since traffic was transferred to the newly launched Satcom III and IV satellites.

EFFECTIVIVITY OF RECONDITIONING ON NICKEL-CADMIUM CELLS USED IN LOW EARTH ORBIT APPLICATIONS

TIROS "N" and NOAA "A" flight lot cells were tested at the Naval Weapons Support Center, Crane (Reference 3) under low earth regimes. They were designated packs 26G and 26H, with 5 cells in each pack at start of the test. Both packs were cycled at 10°C, the former at 20% DOD and the later at 25% DOD. Selected cells from each pack received a capacity discharge cycle to 0.75 volts at predetermined time intervals as follows:

- o Cell 1 - every 6 months
- o Cell 2 - every 12 months
- o Cell 3 - every 18 months
- o Cell 4 - every 24 months

After 42 months the capacity cycles were discontinued on all cells.

The test regime and pack voltage data have been reported in Reference 3. The cell design details, precycling and capacity data were reported in Reference 4. The individual cell voltage data reported herein were obtained by private communications with NWSC, Crane.

Each capacity cycle is equivalent to a reconditioning cycle. Reconditioning appears to be more beneficial if the discharge is terminated at a very low cell potential and close to zero volts. Therefore, any reconditioning effects observed in these tests are of interest for trending only and do not represent optimized and minimized cell voltage degradation values with cycle life.

Figure 4 shows the individual cell end-of-discharge (EOD) voltages for pack 26G at selected cycles from cycle 6000 through 9200. Basically, the end-of-discharge (EOD) voltages for all cells form two distinct curves; the upper for cells previously capacity cycled and the lower for non-capacity cycled cells since the start of this test. Since cells 1 and 2 were already capacity cycled prior to cycle 6000 they form the upper curve and cells 3, 4 and 5 form the lower. Following the capacity test at 18 month, the EOD for cell 3 rises from the lower into the upper curve. The very same trend can be observed for the cell's EOD voltage on pack 26H for the same cycle region (6000-9200). This is shown in Figure 5. All cells in this group, however, had received an non-scheduled capacity cycle at cycle 6812 when the control unit malfunctioned. As a consequence their EOD values rose to those in the upper curve. Subsequent to this non-scheduled capacity cycle there was a gradual EOD voltage decline on those cells which had received no regularly scheduled capacity cycles.

Figure 6 shows the EOD cell voltages from pack 26G starting from cycle 10,000 through 22,681 (obtained on 9/30/82 - latest furnished). The EOD cell voltage trend is a little more complex for these later cycles. Again the top curve is formed by cells which had received the largest number of prior capacity cycles. Consistently, a cell's EOD voltage after it had received a capacity cycle reaches the top curve. It is of interest to note that the top curve value of 1.224 volts as achieved at approximate cycle 6000 (see Figure 4) is reached again after approximate 11,400, 15,600 and 18,600 cycles, respectively. Thereafter, the capacity cycles were discontinued on all cells and a general EOD voltage degradation can be noted. At approximate cycle 15,520 the EOD voltage for cell 3 started to degrade at a relatively faster rate than the others. It had not received a capacity cycle for the prior 12 month period. A similar trend can be noted on cell 4 shortly after the 42 month period. It had not received a capacity cycle for the prior 18 month period. The only exception to this trend is the EOD voltage for cell

5. It had not received any capacity cycle since the start of this test. Its EOD voltage started to increase at about cycle 13040 for a yet unexplained reason. This cell and cell 5 from the pack 26H were removed from their tests after 34 months of testing for a destructive analysis. Those results were previously reported in Reference 3.

A similar EOD voltage trend to those described previously can be noted in Figure 7. It shows the pack 26H EOD voltage data from cycle 10,000 through 22,743. Cell 5 in this pack follows the general trend of observed lower EOD voltages, on those cells which had received no or a minimal number of reconditioning cycles. It had received one prior non-scheduled capacity cycle on cycle 6812 and showed a steady EOD voltage decline since. Toward the later portion of this test, cell 3 showed a considerable EOD voltage decline after the percent return (ampere-hour input divided by ampere-hour output times 100) was reduced from 119% to 110% (cycle 22305). It had shown, however lower end-of-charge voltages indicating some unbalance between this cell and the others existed. It should be noted here that in general the percent charge return was low in both packs; for pack 26G it ranged from 101 to 110% for most cycles and for pack 26H it ranged from 102 to 106% for most cycles. This low charge return appears to have caused an occasionally observed cell unbalance on those cells which are slightly less efficient. This effect appears to be more pronounced during later cycle life.

CONCLUSIONS

1) On RCA Geostationary Battery In-Orbit Performance

Both Satcom F1 and F2 batteries reported herein have been operating successfully in orbit for about 7 and 6-3/4 years, respectively. Their end-of-discharge voltage degradation with increase in eclipse seasons has been minimal for approximately equal depth-of-discharges. This degradation is considerably lower than predicted. This can be attributed to a large extent to the unique RCA Astro reconditioning procedure applied prior to each eclipse season.

2) Trend of Effect of Reconditioning on Nickel Cadmium Cells on Low Earth Orbit Applications

A strong trend for a long duration effect of reconditioning can be noted on nickel-cadmium cells used for low earth applications. Cells which have been periodically capacity discharged during their cycling show that they have maintained higher end-of-discharge voltages than those not capacity cycled over their long term cycling of almost 4 year duration

RECOMMENDATIONS

On Effect of Reconditioning of Nickel Cadmium Cells Used on Low Earth Applications

Further investigations should be directed toward the applicability of reconditioning of nickel-cadmium cells to reduce end-of-discharge voltage degradation and thereby increase mission life. This would become feasible in programs where multi-batteries exist on each spacecraft. It has been generally observed and reported that a reconditioning discharge to a very low cell voltage is the most effective technique. The RCA Astro unique reconditioning circuitry, so effective in geostationary applications, is well suited to accomplish this. It can achieve this within a short time period which is especially desirable since cycles occur very frequently. It has shown very reliable performance, is of light-weight and will prevent cell reversals during this reconditioning.

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MINIMUM AVERAGE BATTERY VOLTAGE VS NUMBER OF ECLIPSE SEASONS

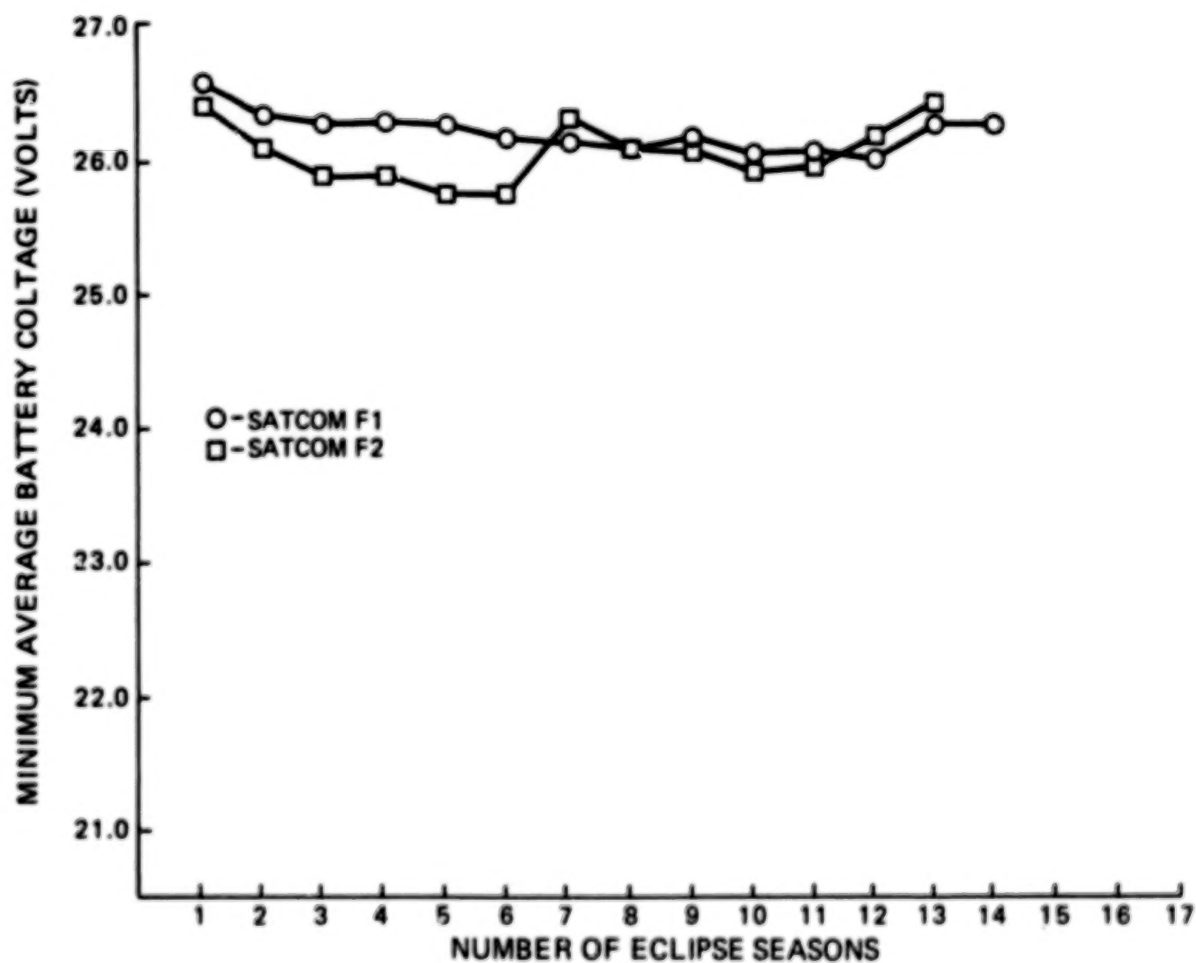


Figure 1

MINIMUM AVERAGE CELL VOLTAGE DURING ECLIPSE VS NUMBER OF ECLIPSE SEASONS

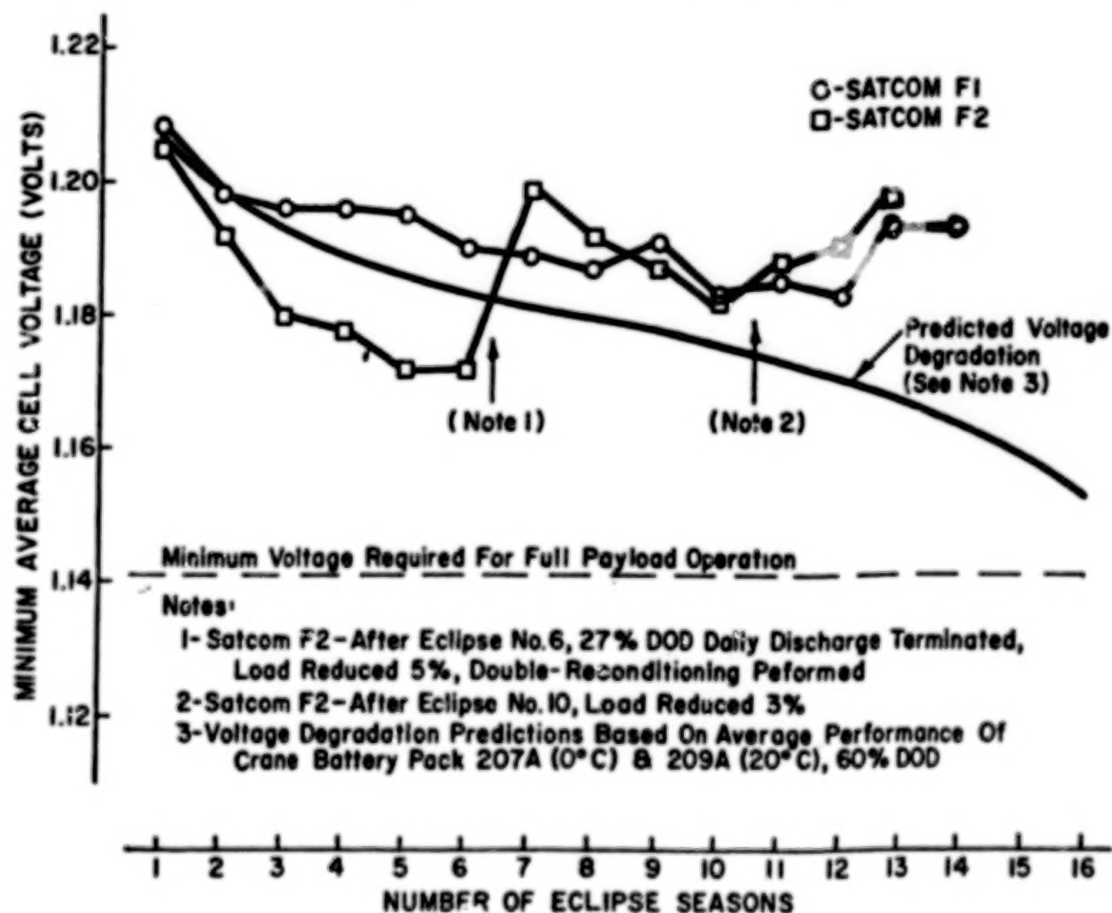


Figure 2

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MAXIMUM AVERAGE DEPTH-OF-DISCHARGE DURING ECLIPSE
VS NUMBER OF ECLIPSE SEASONS

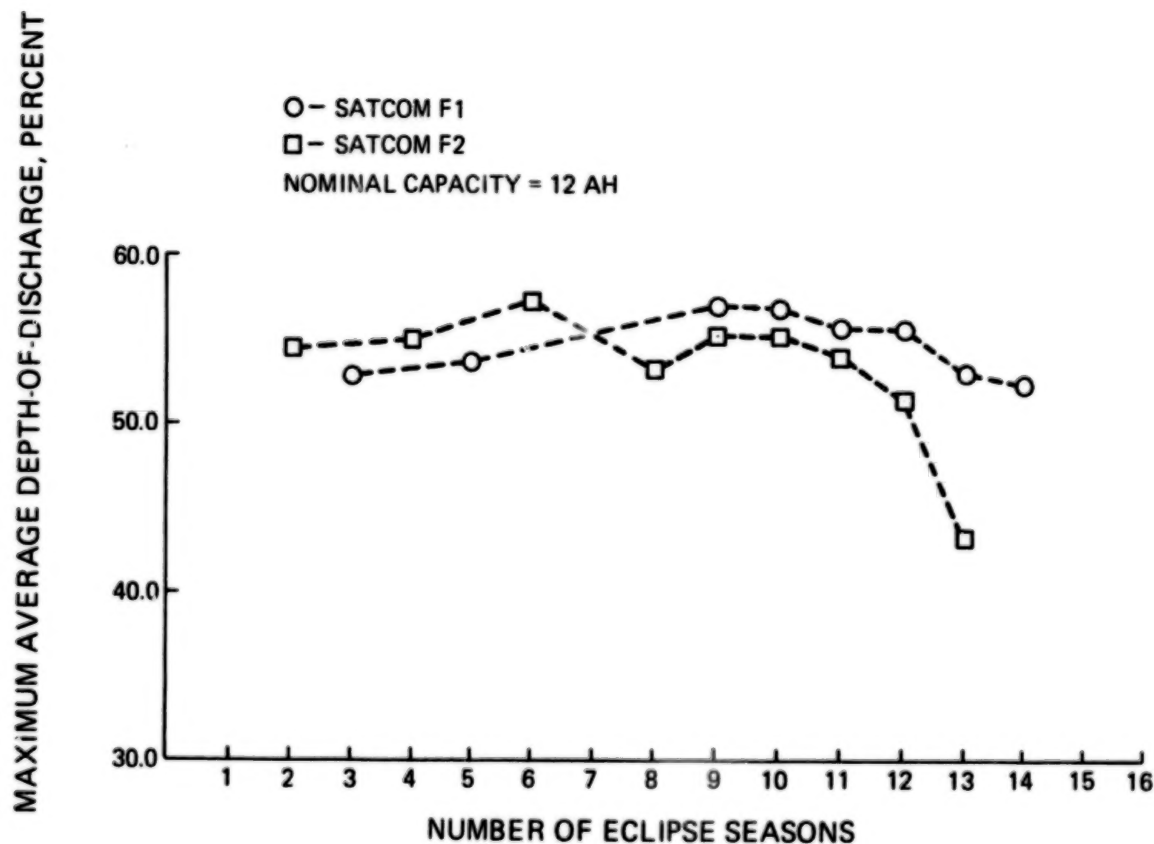


Figure 3

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END-OF-DISCHARGE VOLTAGE VS CYCLE NUMBER FOR PACK 26G CELLS 20% DOD, 10°C

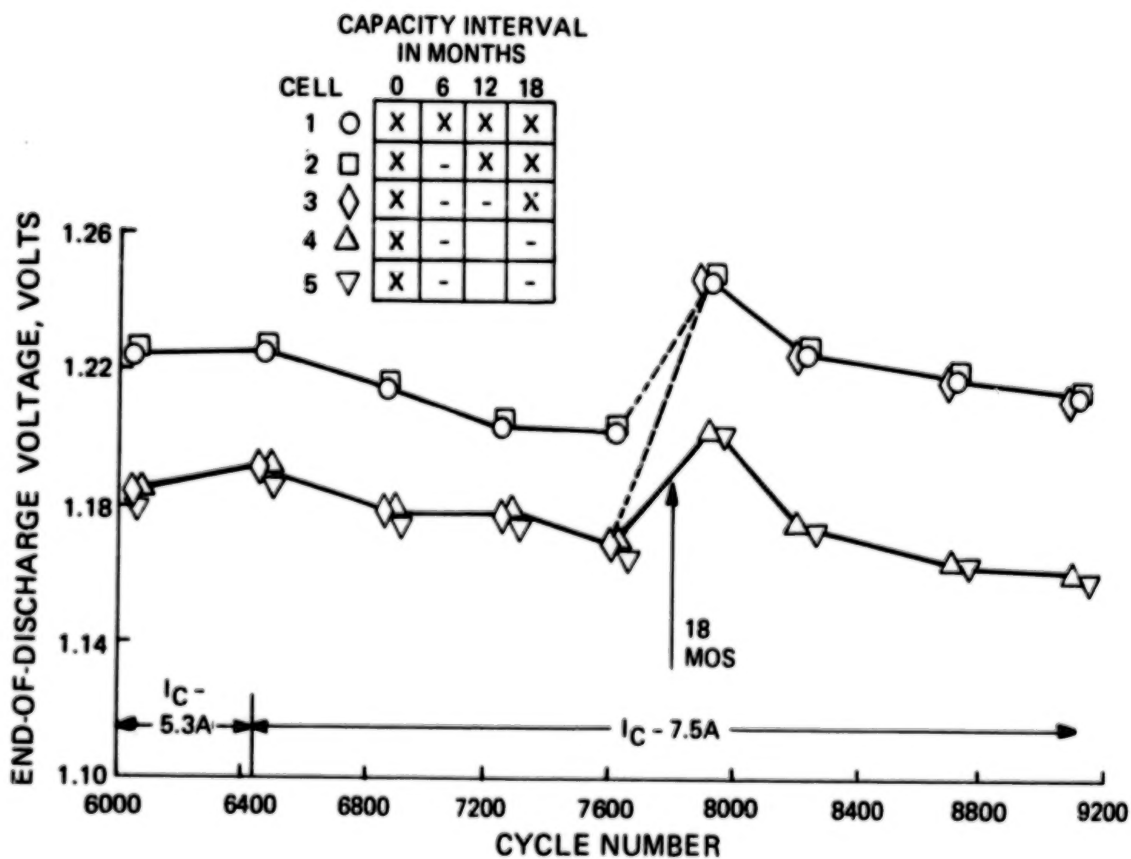


Figure 4

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END-OF-DISCHARGE VOLTAGES VS CYCLE NUMBER FOR PACK 26H CELLS 25% DOD, 10°C

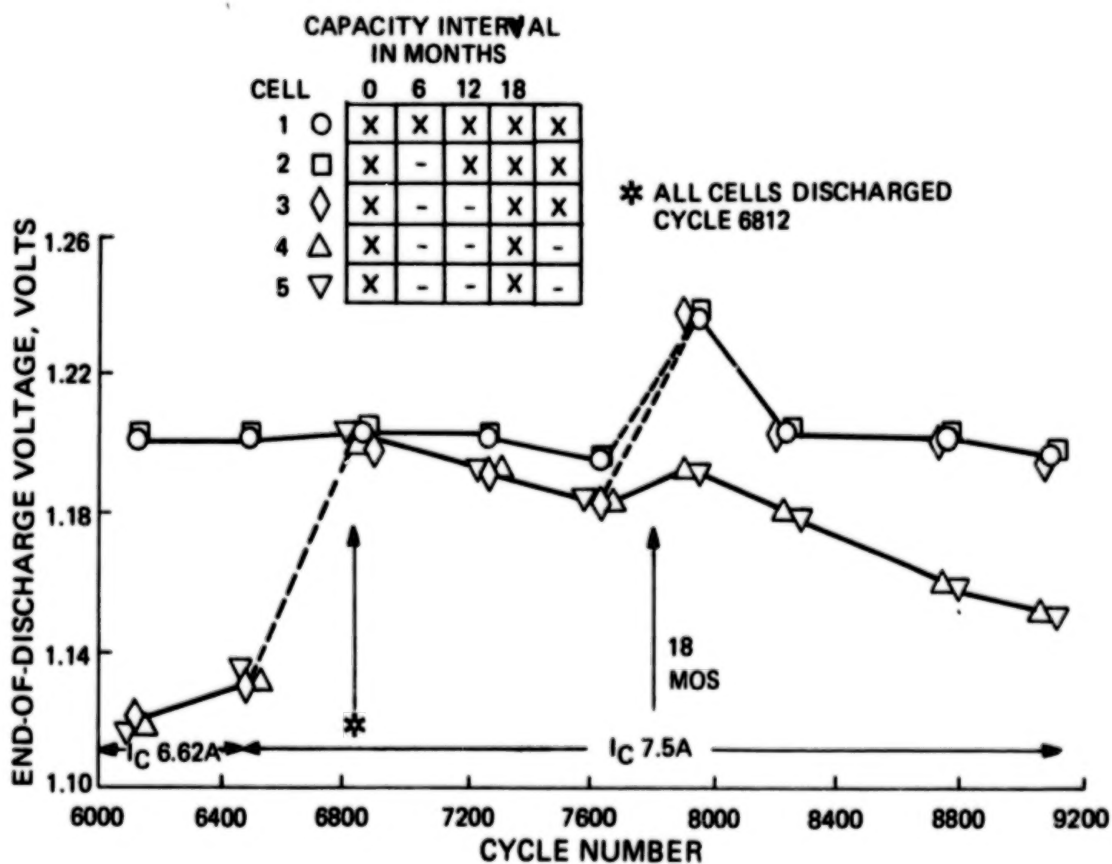


Figure 5

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END-OF-DISCHARGE VOLTAGE VS CYCLE NUMBER FOR PACK 26G CELLS 20% DOD, 10°C

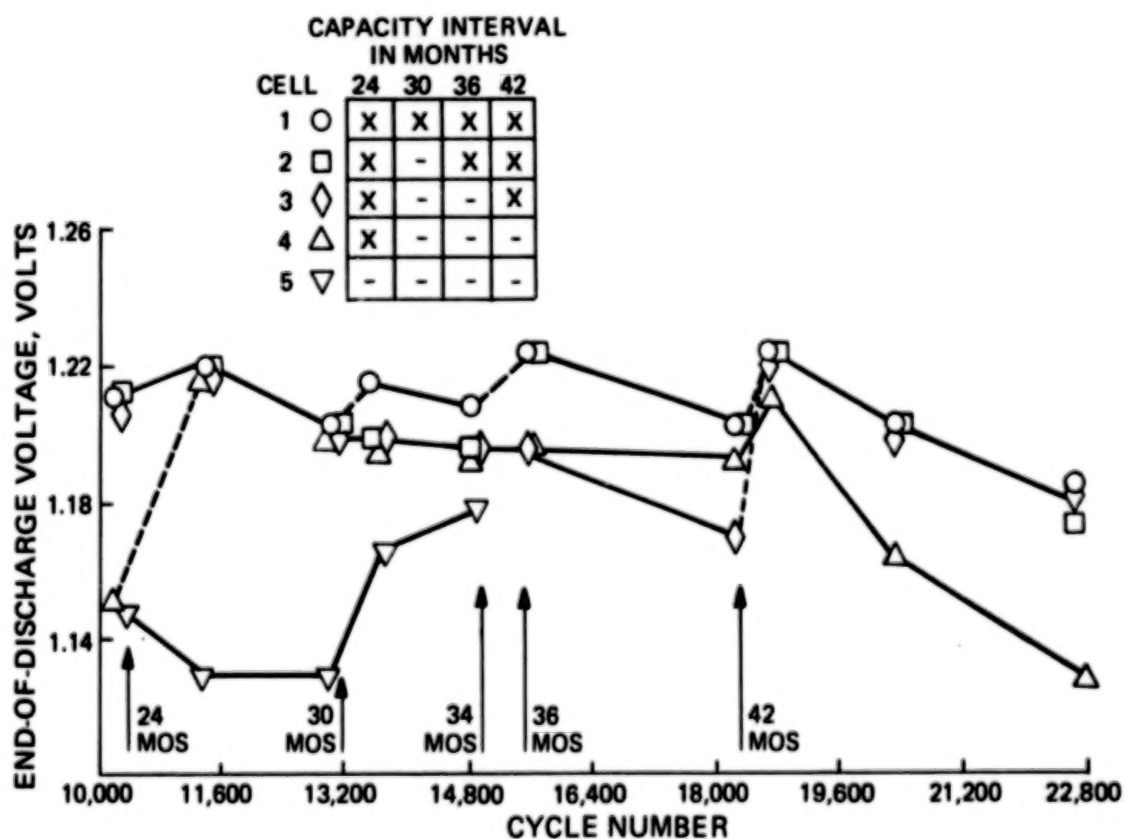


Figure 6

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END-OF-DISCHARGE VOLTAGES VS CYCLE NUMBER FOR PACK 26H CELLS 25% DOD, 10°C

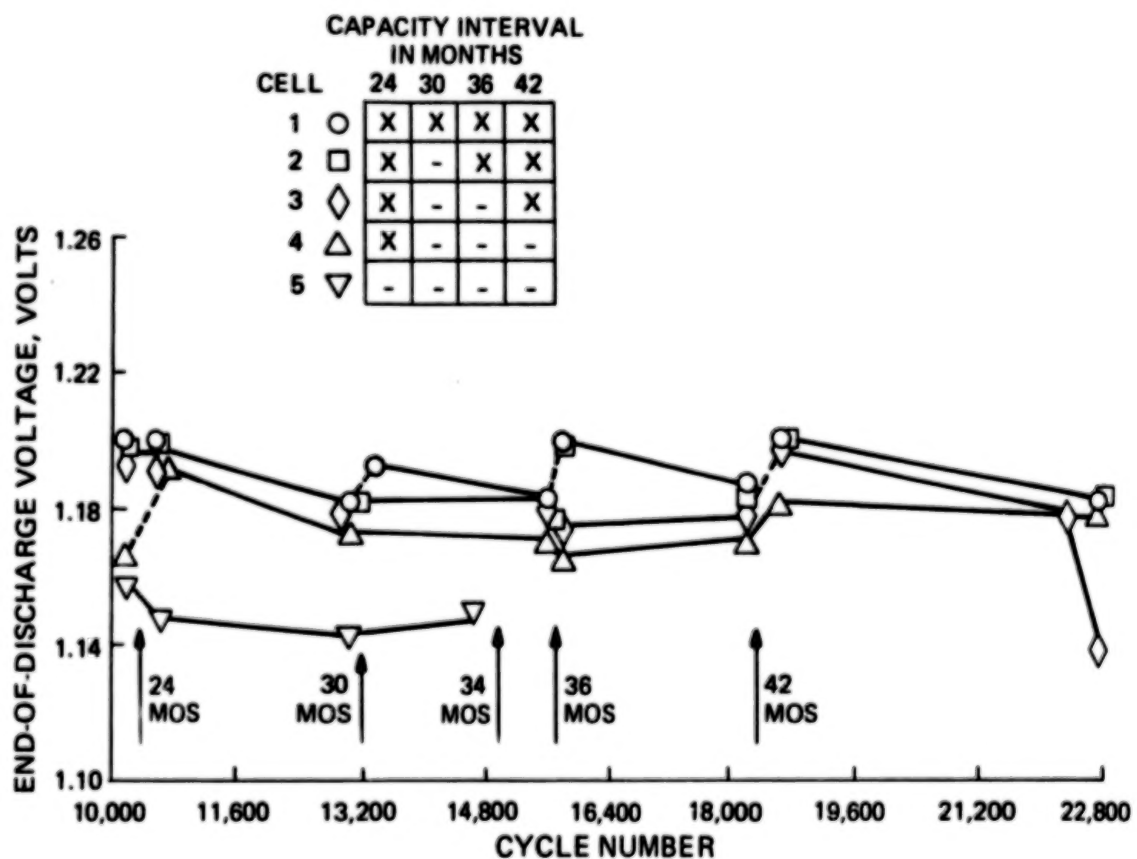


Figure 7

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ACKNOWLEDGEMENTS

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RECONDITIONING AND THE NICKEL ELECTRODE

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ABSTRACT

The effects of reconditioning on the performance of NiCd batteries are reviewed. These effects are correlated with cell experiments and individual electrode investigations. The effects of reconditioning on the positive electrode performance are found to be significant. A mechanism is proposed that rationalizes the operation of the nickel electrode and suggests that reconditioning minimizes depth of discharge stress during use and maintains uniformity of the active material.

INTRODUCTION

Data from ground testing and flight indicate that reconditioning is effective in both the short and long term for maintaining both the voltage and reserve capacity performance of NiCd batteries in high orbit vehicles. Deep discharge reconditioning to voltages of less than 1.0 V/cell may be sufficiently effective as to enable power systems to employ NiCd batteries and depths of discharge (DOD) well over 50 percent for long duration synchronous orbits. Risks associated with deep discharge reconditioning do not appear to be unacceptably high. Analysis of test results and other data suggest that reconditioning of NiCd batteries in low orbits may also extend the operational life of the batteries. Finally, data suggest that NiH₂ batteries used in high orbits maintain performance better if they are reconditioned.

We will discuss reconditioning on a battery basis and its effects on performance. The results of individual cell testing will be described. Finally, studies of the positive electrode will be presented that illustrate the origin of many of the effects observed.

BATTERY LEVEL OBSERVATIONS

Reconditioning increases the voltage at which a NiCd battery delivers capacity by removing the voltage decrease that results from cycling. This has the effect of increasing battery capacity because a battery can develop voltage depressions of a few tenths of a volt per cell. From our view, sufficiently deep, periodic reconditioning not only affects near term voltage in a favorable way but provides long term maintenance of capacity and thereby provides higher reliability at longer mission lives.

Deep discharge appears to be most effective as has been shown by ground test and now by some vehicle data(1,2) Figure 1 compares the data for shallower and deeper reconditioning. Note that both of these curves are for missions that will easily reach planned life based on extension of these curves. The risks associated with deep discharge reconditioning on a battery basis, that is, a dangerous build-up of hydrogen pressure and an increased risk of cell failure from shorting caused by cell reversal, have not been demonstrated for cells and batteries tested by others^{3,4,5} or ourselves^(6,7,8). These conclusions do not necessarily apply to degraded, older cells that have not been properly reconditioned.

RECONDITIONING DATA FROM CELLS

Our studies at the cell level have been performed on both relatively new (fewer than 100 cycles) and relatively old (more than 7 years and more than 500 cycles) cells and laboratory cells made from aerospace components. Absolute values of the data do vary from cell to cell however, qualitatively, the data are all in agreement. Cell tests are not life projections but rather performance data that show short term effects of reconditioning (9) These data, when coupled to battery and electrode studies reveal much about the effects of reconditioning.

When a cell is cycled, the discharge voltage at any given state of charge decreases. The capacity available at any usable voltage also decreases as shown in Figure 2. The factors affecting the voltage loss, ΔV , were evaluated. The results are shown by plotting the voltage

loss (the difference between the voltage observed and that for the cell after reconditioning when discharged in exactly the same way) against the parameter being evaluated. Figure 3 gives the voltage loss as a function of depth of discharge at discharge rates of 0.4 and 0.05 C following 37, 40 percent DOD cycles. The data indicate that there is a resistive, rate dependent component and a loss in voltage related to the thermodynamics of the cell (E°). Figure 4 shows that the voltage loss at the 40% DOD point is independent of discharge rate when the same depth of discharge is reached over the range C/7 to C. Conversely, voltage loss is more dependent on the charge rate as shown in Figure 6 for 12 and 29 cycles of 40 percent DOD. The rates indicated are for charging to 80 percent charge return at the rates indicated followed by a C/10 rate for complete charge to 125 percent return. High rate charge results in less voltage loss and a lower rate of loss than low rate charge; this suggests the reason why low earth orbit conditions may not require reconditioning or, at least, less frequent reconditioning. Although low rate overcharge has little effect on the voltage loss, long durations at higher rates (C/10 and greater) cause the voltage depression to increase markedly. Extensive high rate overcharge results in a depressed, but very flat discharge curve. Finally, the dependence of the voltage on the depth of discharge as a function of the number of cycles is shown in Figure 6. The range of 10 percent to 80 percent DOD has little effect on the voltage loss except for the lowest DOD which possibly shows as much as 20 percent less depression after about 20 cycles.

The voltage loss is composed of a term that is independent of the rates of charge, discharge, or DOD and requires 15 to 25 cycles to reach a stable value. A second term is rate dependent. Equation 1 shows the relationship,

$$\Delta V = I_d \Delta R_{\text{eff}} + \Delta V_o$$

The discharge current, I_d , causes a voltage depression because of ΔR_{eff} that is added to the thermodynamic component ΔV_o . The magnitude of the rate dependent coefficient is dependent only on the number of cycles and the

charge rate. This coefficient, ΔR_{eff} , is not a purely resistive term; several of the figures show that ΔV is dependent on a term containing higher powers of current than the linear IR_{eff} dependence.

Short term reconditioning effects are an increase in voltage and capacity to a usable voltage for a net increase in available watt-hours. The ampere-hour capacity of a properly functioning cell remains approximately the same at all times. However, the discharge voltage required to recover that capacity can be very low. We have examined the effects of reconditioning under several conditions on a single cell basis.(10)

A cell was cycled 37 times at 40 percent DOD then various reconditioning procedures were applied. Reconditioning rates of C/100, C/20, C/4 and C/2.5 were employed after the cell was discharged to 1.1 V at C/2.5. Single and multiple R/D cycles were evaluated. The reconditioning cut-off voltages were 1.1 V and 0.01 V. The data compared were the time-integral average discharge voltage and the capacity to 1.1 V at C/2.5 for the discharge cycle that began the R/D and for the subsequent discharge of the reconditioned cell.

Figure 7 shows the recovery of capacity and voltage as a function of reconditioning rate. Capacity and voltage recovery are, of course, most significant at lower rates to lower voltages. Capacity can be recovered by a single, low-rate deep cycle or by multiple shallow cycles at low rate. Increased voltage recovery continues for multiple cycles, even at the lowest rate and cut-off voltage. The differences in the capacity and voltage recovery dependence are the result of recovery of nearly all capacity to above 1.1 V rapidly whereas voltage improvements above 1.1 V continue for several cycles. Complete recovery of the voltage may not be important in the short term because of the rapid but limited loss of voltage during subsequent discharges.

The differences in voltage and capacity recovery and the use of batteries under constant power conditions suggests that a better figure of merit for reconditioning would be recovery of watt-hours. The relative improvements for the voltage, capacity and energy (overall) for the various

reconditioning procedures are summarized in Table 1. These short-term evaluations do not provide direct data on any improvements in life that might be derived from reconditioning. However, the greater the watt-hour output of the battery, the lower the DOD and current in many systems and the lower the overcharge experienced by the cell. These conditions result in a more benign long term battery environment and, presumably, longer life.

RECONDITIONING EFFECTS ON THE NICKEL ELECTRODE

The changes observed in NiCd cells upon cycling and the recovery of the losses in voltage and usable capacity are the result of changes in the positive electrode as shown in Figure 8. Again the loss in voltage is plotted for a laboratory cell containing a reference electrode. The only significant change is in the positive electrode for the typical, positive limited cell. Changes in the negative, although visually evident, do not cause detectable changes in the cell performance under typical spacecraft use conditions.

The mechanism of discharge of a nickel electrode is suggested from Figure 9. The discharge of a sintered nickel electrode and the change in voltage in response to a small current step as a function of the square root of time are shown. The kinetics are diffusion controlled on the upper voltage plateau at a and are attributed to solid state diffusion of protons.⁽¹¹⁻¹⁴⁾ In the low rate plateau region near b mixed kinetics involving both diffusion and activation control the discharge. Finally the discharge is controlled by the electrical conductance of a semiconductor with decreasing carrier density^{15,16} at c. The impedances of these regions are shown in Figure 10 for the different conditions of region, a, b, and c. Under certain experimental conditions as much as 50 percent of the capacity can be in the low voltage plateau region of c.

Figure 11 shows the electrode capacitance in the residual capacity region as a function of capacity discharged for a reconditioned electrode, one cycled 32 times and for a new flat plate electrode. The abruptness of the change in capacitance in the transition from the high to low potential

region is thought to be a measure of the uniformity of the electrode discharge. Thus the flat plate electrode shows a sharp transition but the sintered electrode degrades to no step at all after 32 cycles. This measure of capacitance in the residual capacity region may prove to be an important monitor of the condition of nickel electrodes. Monitoring the capacitances as a function of cycling during reconditioning discharges can predict the onset of the low voltage region and the loss of useful capacity as well as permit correlation of electrode uniformity with performance.

SUMMARY

The control of the operation of NiCd (and NiH_2) cells by the nickel electrode strongly suggests that reconditioning is most effective in maintaining this limiting electrode. The commonly accepted charge-discharge mechanism of the electrode shown in Figure 12 suggests that reconditioning controls the phase composition of the electrode. Complete discharge at low rates also maintains the uniformity of the electrode and prevents build-up of residual capacity. Perhaps key to long term performance is the removal of nonuniformities in the electrode. A build-up of areas that will not participate in cycling causes higher stresses in the cell because the remaining active material will segregate from the non-cycling material and because of the greater depth of discharge in the remaining active material. Obviously, deepest reconditioning can free more material for turn-over in the cycling process. This will have the short term effect of maintaining discharge voltage longer after reconditioning in addition to the maintenance of capacity over longer mission durations.

In the short term, reconditioning serves to maintain discharge voltage and capacity. Discharge at low rate to low voltage is most effective in maintenance of voltage and capacity. Risks associated with deep reconditioning, after some cycling, appear acceptable for low rates. Test and orbital data suggest that reconditioning extends the life of batteries and can permit extension of life at greater depths of discharge. Reconditioning maintains the performance of the positive electrode, however changes do occur in the negative in NiCd cells during reconditioning which

may affect life and performance. We would think that NiH_2 and NiCd will both benefit from reconditioning under similar conditions. Finally the effectiveness and need of reconditioning will depend upon the conditions of battery use.

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Table 1. Relative merit of common reconditioning procedures for short-term maintenance of NiCd cell capacity and voltage.

	<u>Voltage</u>	<u>Capacity</u>	<u>Overall</u>
A. Single low-rate (C/100) cycle, to 0.01 V	0.72	0.99	0.94
B. Two low-rate cycles, to 0.01 V	1.00	1.00	1.00
C. Single low-rate cycle, to 1.1 V	0.59	0.64	0.63
D. Two low-rate cycles, to 1.1 V	0.78	0.81	0.81
E. Single C/10 cycle to 1.1 V	0.43	0.43	0.43
F. Two C/10 cycles to 1.1 V	0.61	0.52	0.54
G. Single Capacity discharge to 1.1 V, C/2.5	0.20	0.19	0.19
H. Single C/10 cycle to 0.01 V	0.71	0.61	0.67

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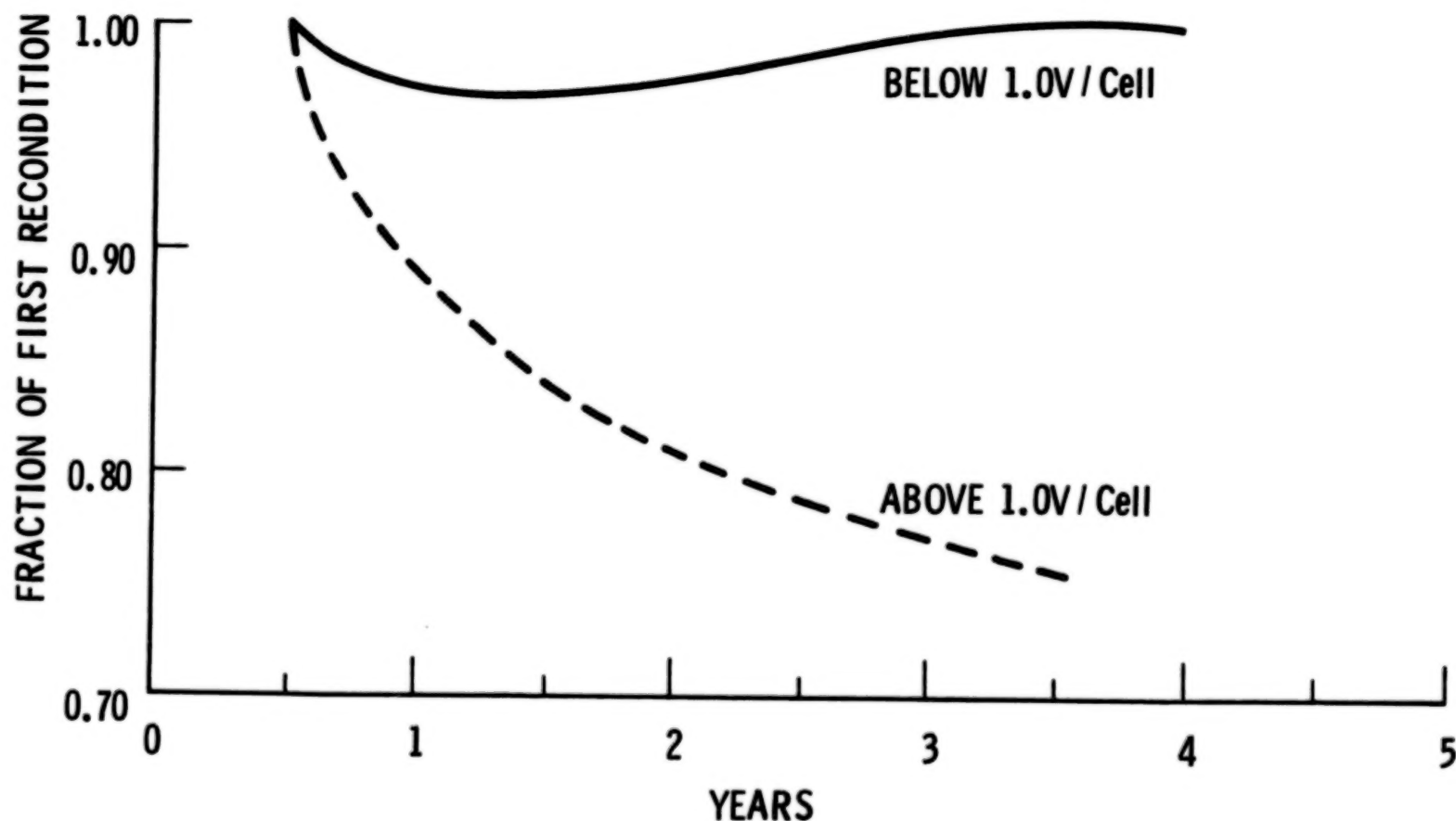


Figure 1. Effect of Depth of Reconditioning on capacity. Solid curve is for reconditioning to below 1.0 V/cell average. Dashed curve is for reconditioning to above 1.0 V/cell average.

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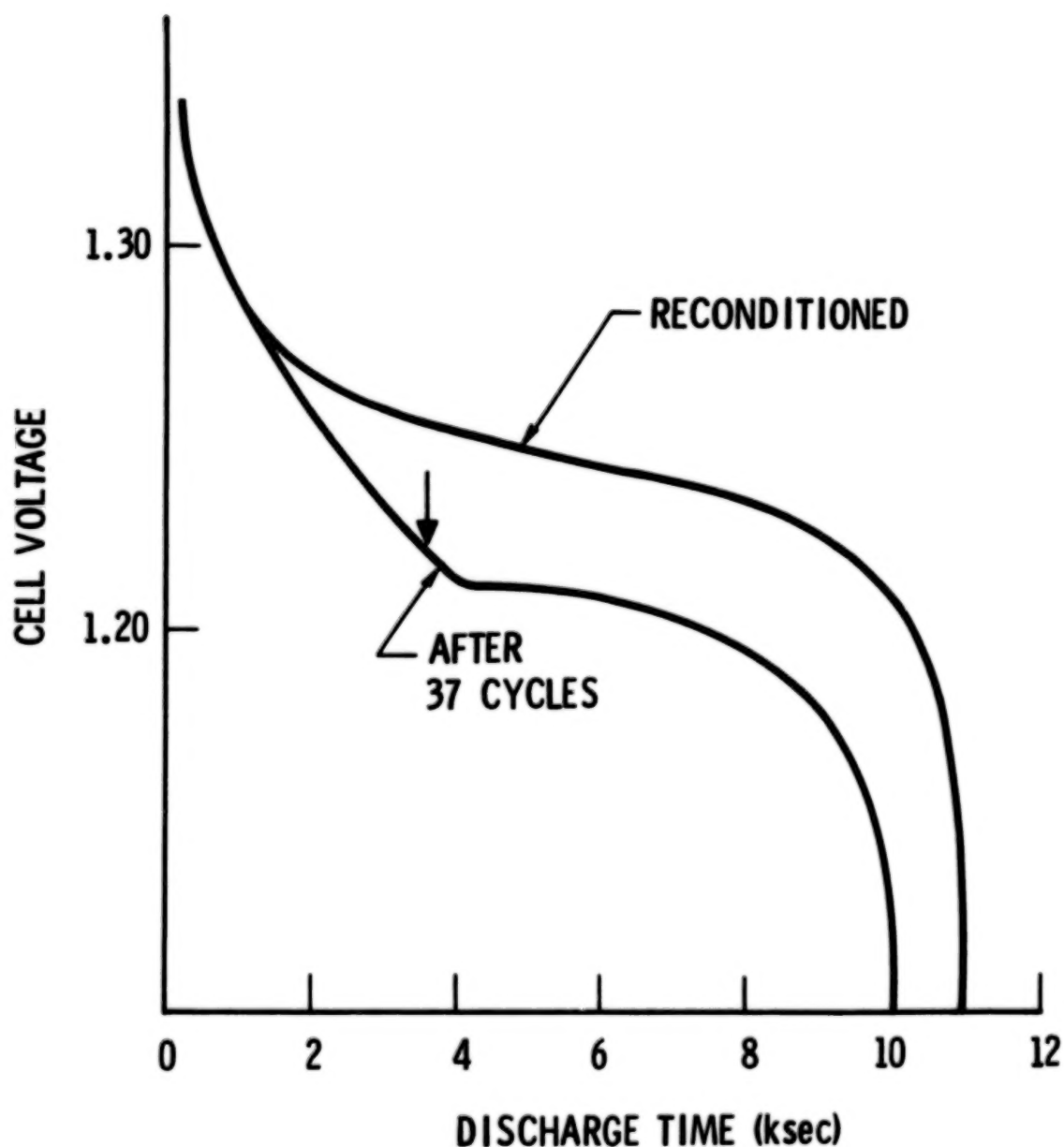


Figure 2. Discharge characteristics of NiCd cell after reconditioning and after 37 cycles; 0.4C discharge (1 h), 0.25C charge (1.28 h) 0.1C charge (1.6 h) for each cycle. The arrow indicates the depth-of-discharge to which the cell was cycled.

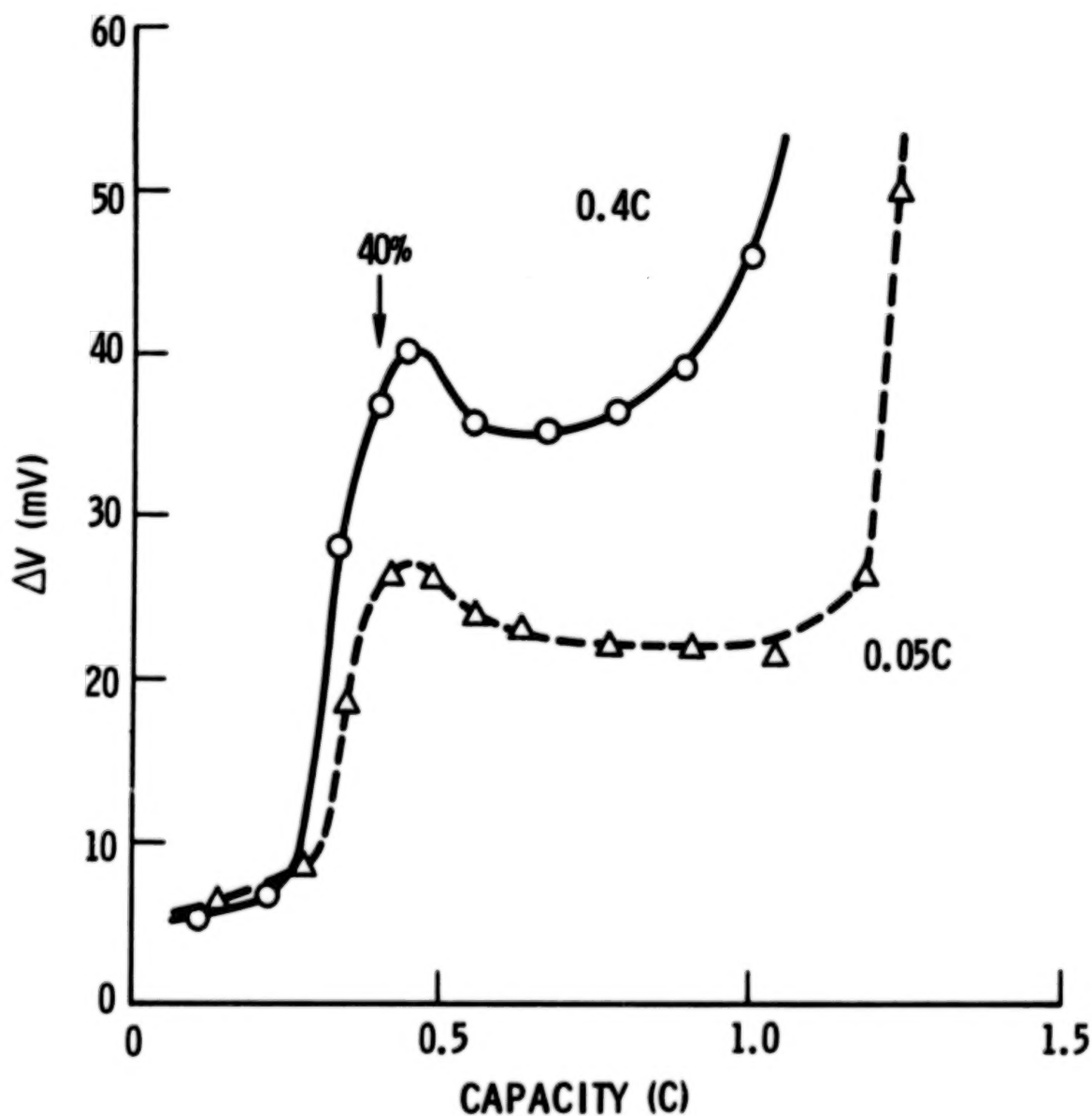


Figure 3. Voltage loss as a function of depth-of-discharge for discharge at 0.4C (circles) and 0.05C (triangles) after 37 cycles as indicated in Figure 2.

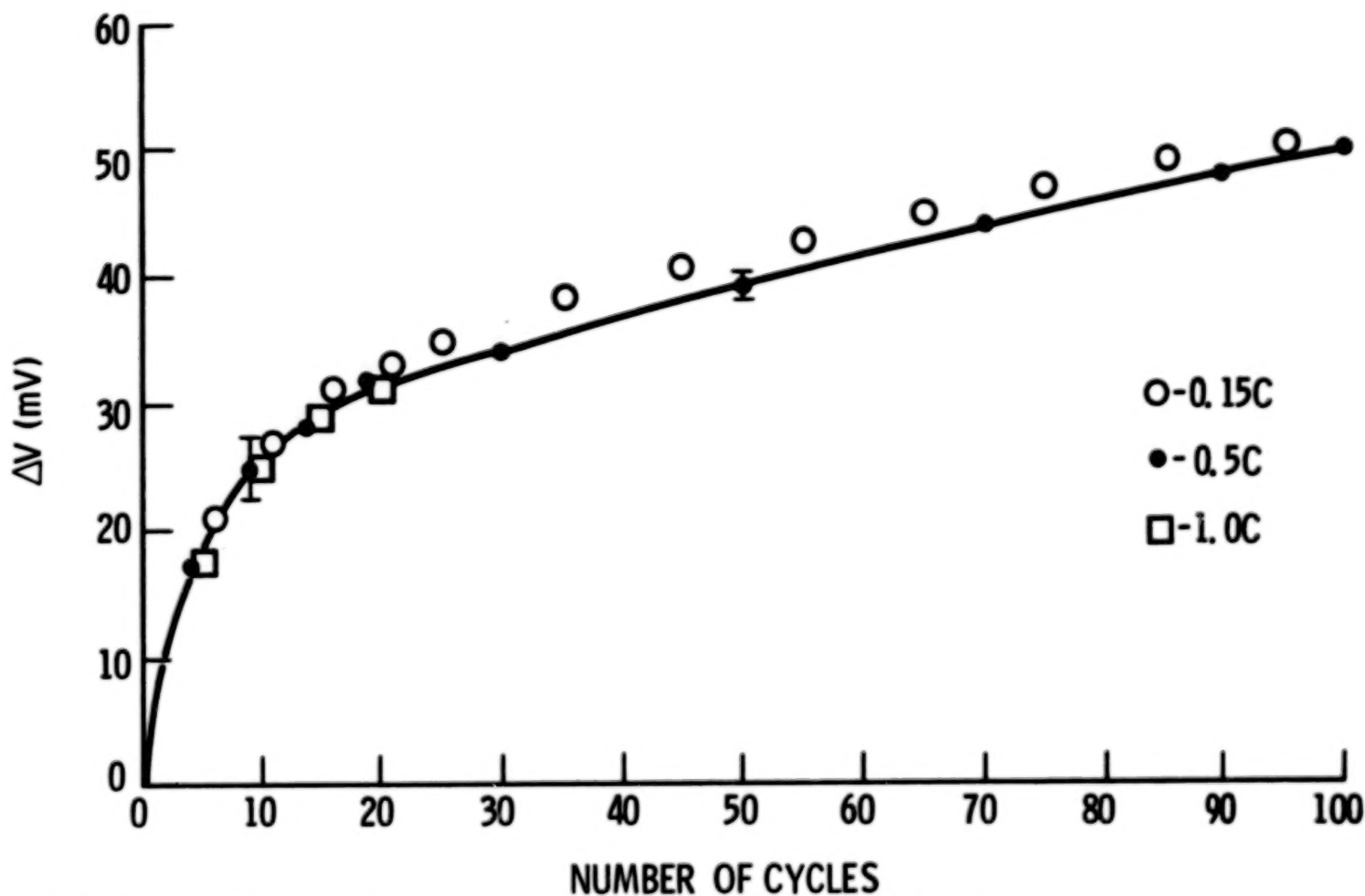


Figure 4. Development of voltage loss with cycling for a NiCd cell at several discharge currents. Each cycle employed 40% DOD, followed by 0.1C charge for 5 h. The discharge currents are indicated in the figure.

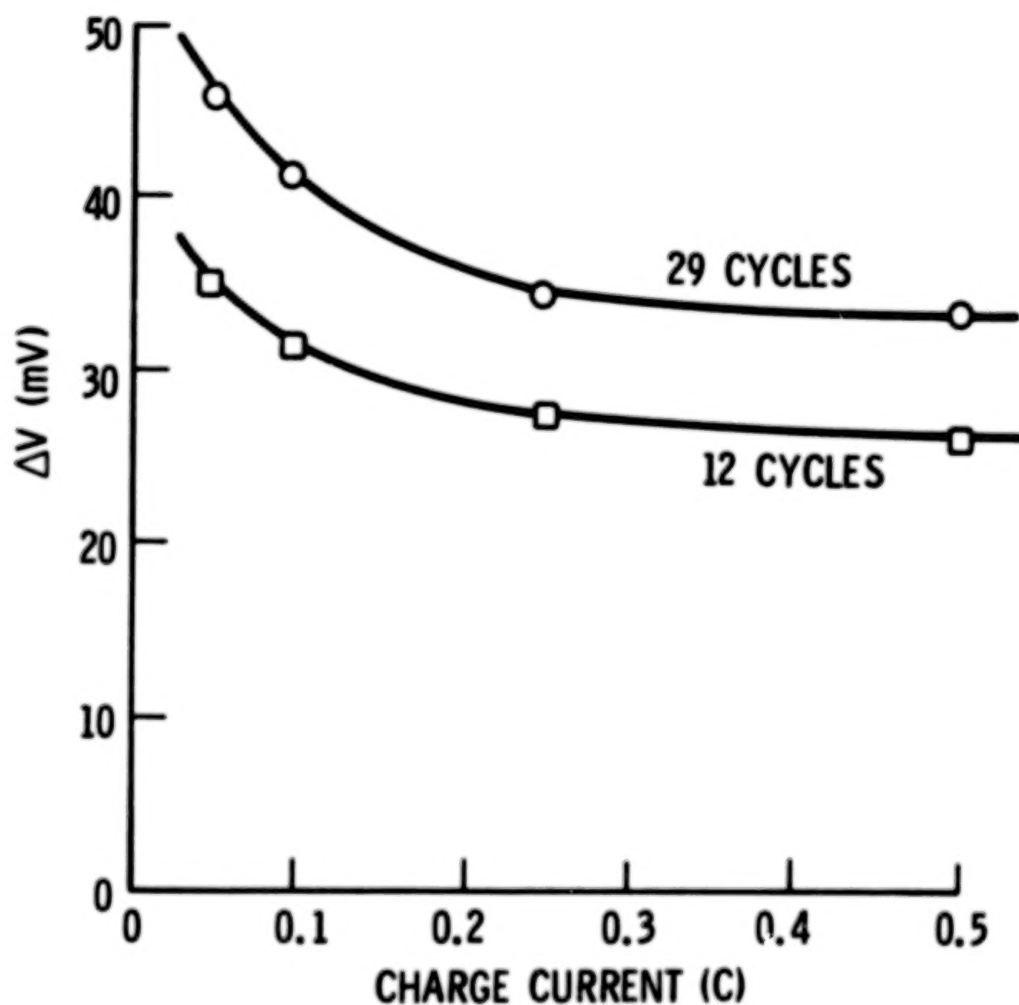


Figure 5. Dependence of voltage loss on the charge current used during cycling; after 12 cycles (squares) and after 29 cycles (circles). Each cycle involved a 0.5C discharge to 40% DOD, followed by recharge at the current indicated on the abscissa for 80% charge return and then at 0.1C to a total of 125% charge return.

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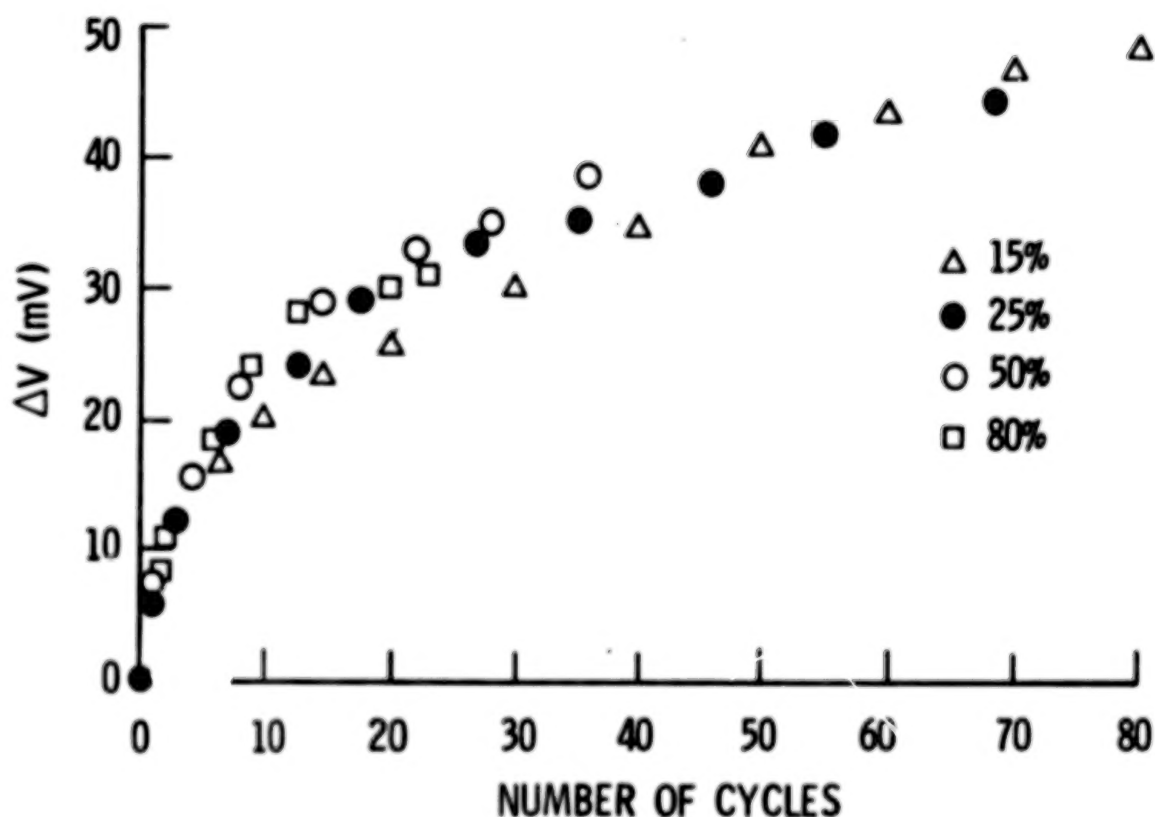


Figure 6. Development of voltage loss for cycling to various depths of discharge. Each cycle involved discharge at 0.5C to 10% (triangles), 25% (points), 50% (circles), and 80% (squares) DOD, followed by recharge at 0.25C until 80% of the capacity discharged was returned, then recharge at 0.1C until 125% of the capacity discharge was returned.

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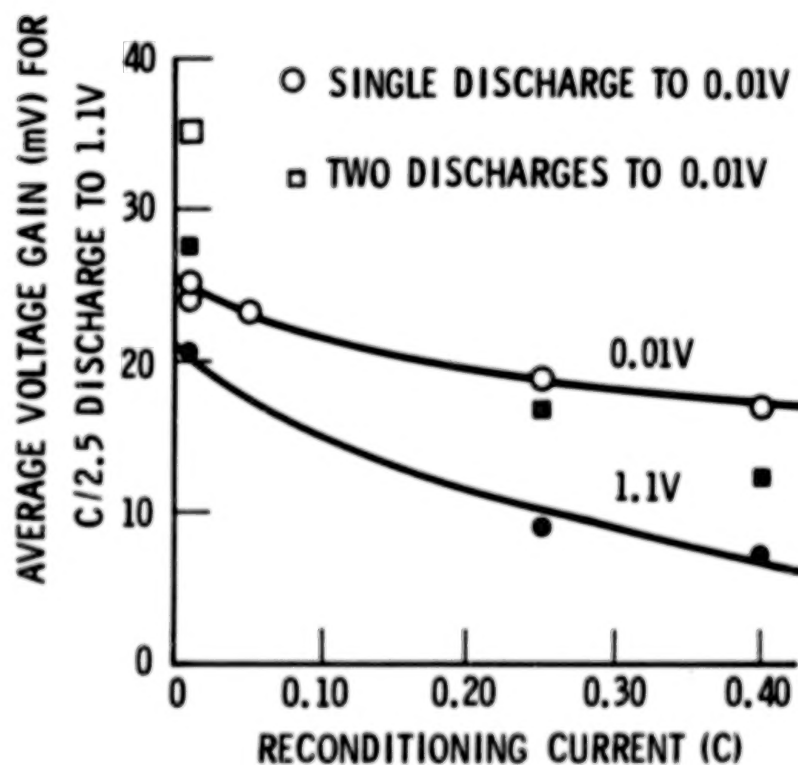
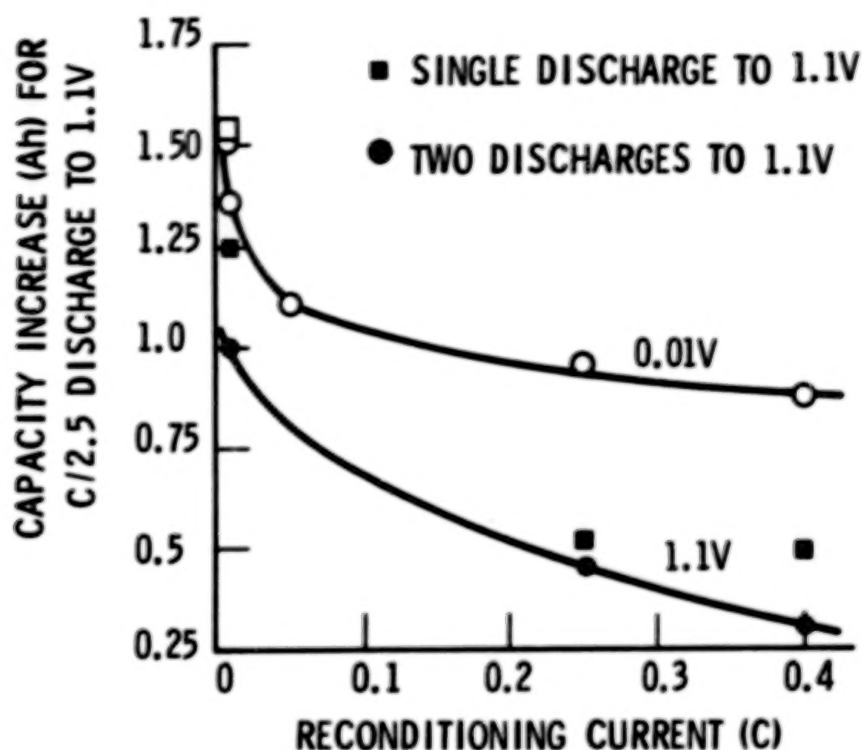


Figure 7. Capacity (top) and voltage (bottom) enhancement from reconditioning of a NiCd cell. The symbol definitions given in the top and bottom figures apply to both figures.

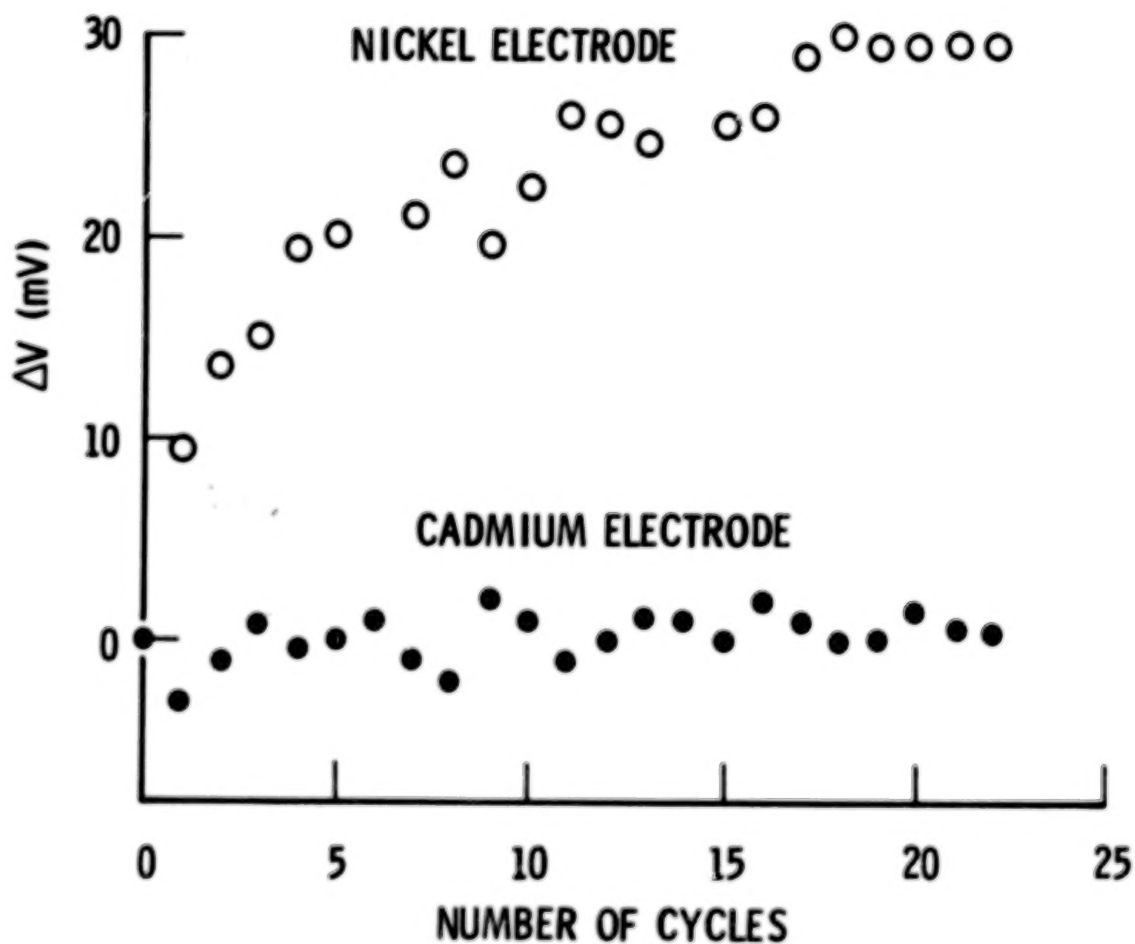


Figure 8. Development of voltage loss with cycling in a 1-Ah NiCd cell at the Ni electrode and Cd electrode. The reference electrode was Ag/Ag₂O. Each cycle involved discharge at 0.15 A for 0.4 Ah followed by recharge at 0.10 A for 0.46 Ah.

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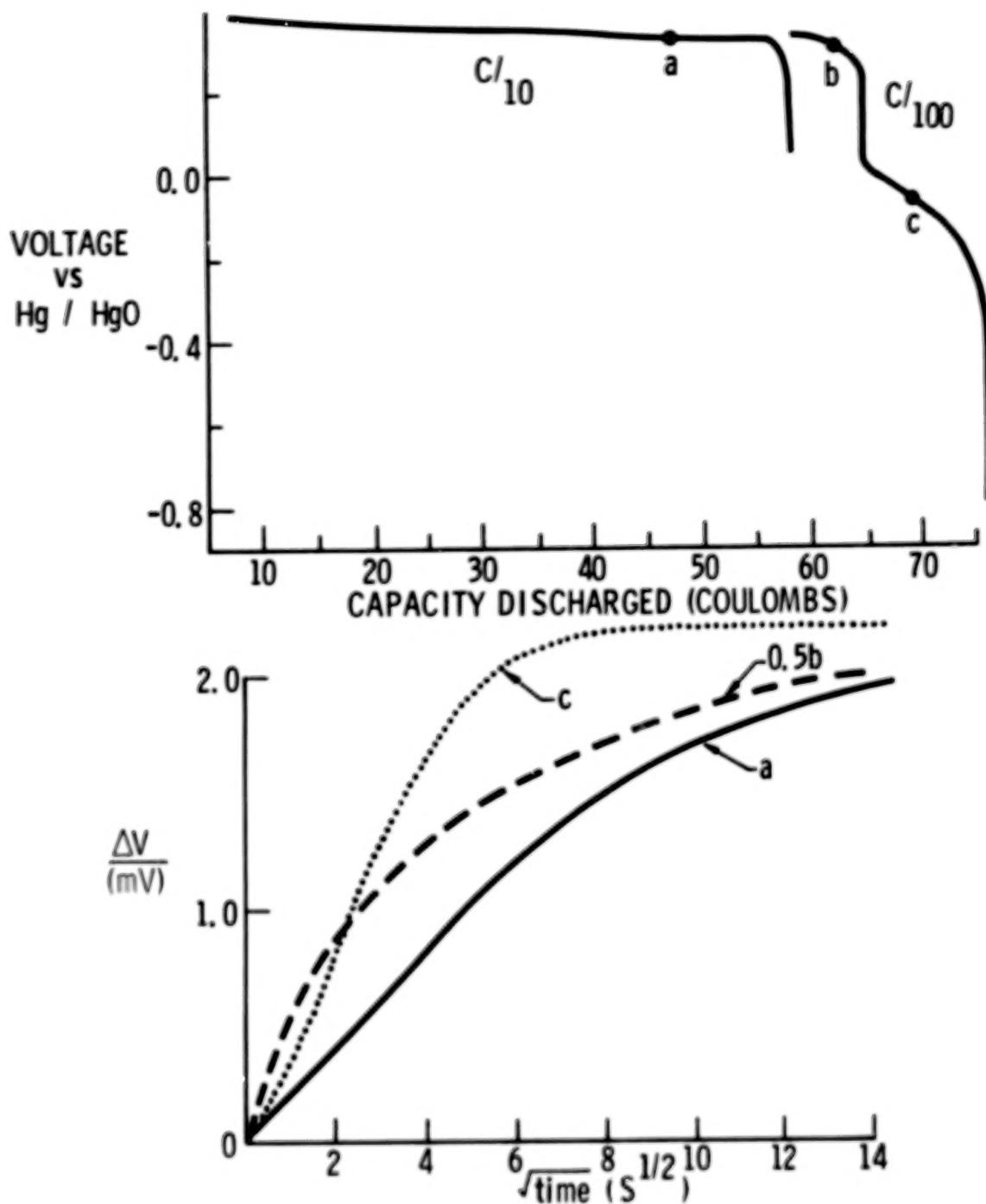


Figure 9. Discharge of a nickel electrode showing three different regions (top). Response of the electrode to a small current step is shown in the lower figure at the points indicated above (bottom).

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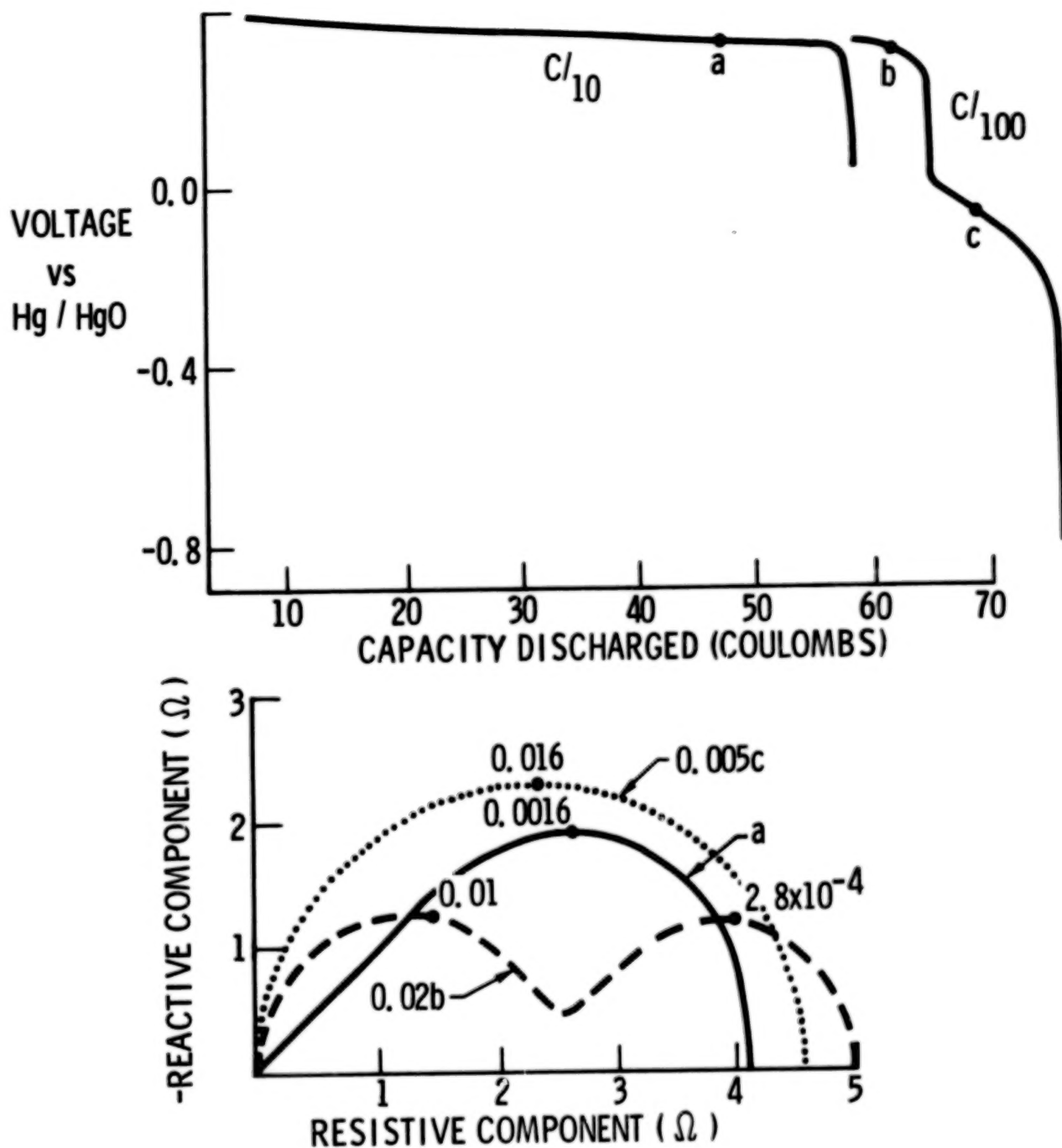


Figure 10. The discharge of a nickel electrode is the same as Figure 9 (top). The impedance of the electrode at the points indicated (bottom). The numbers in the plots are frequencies.

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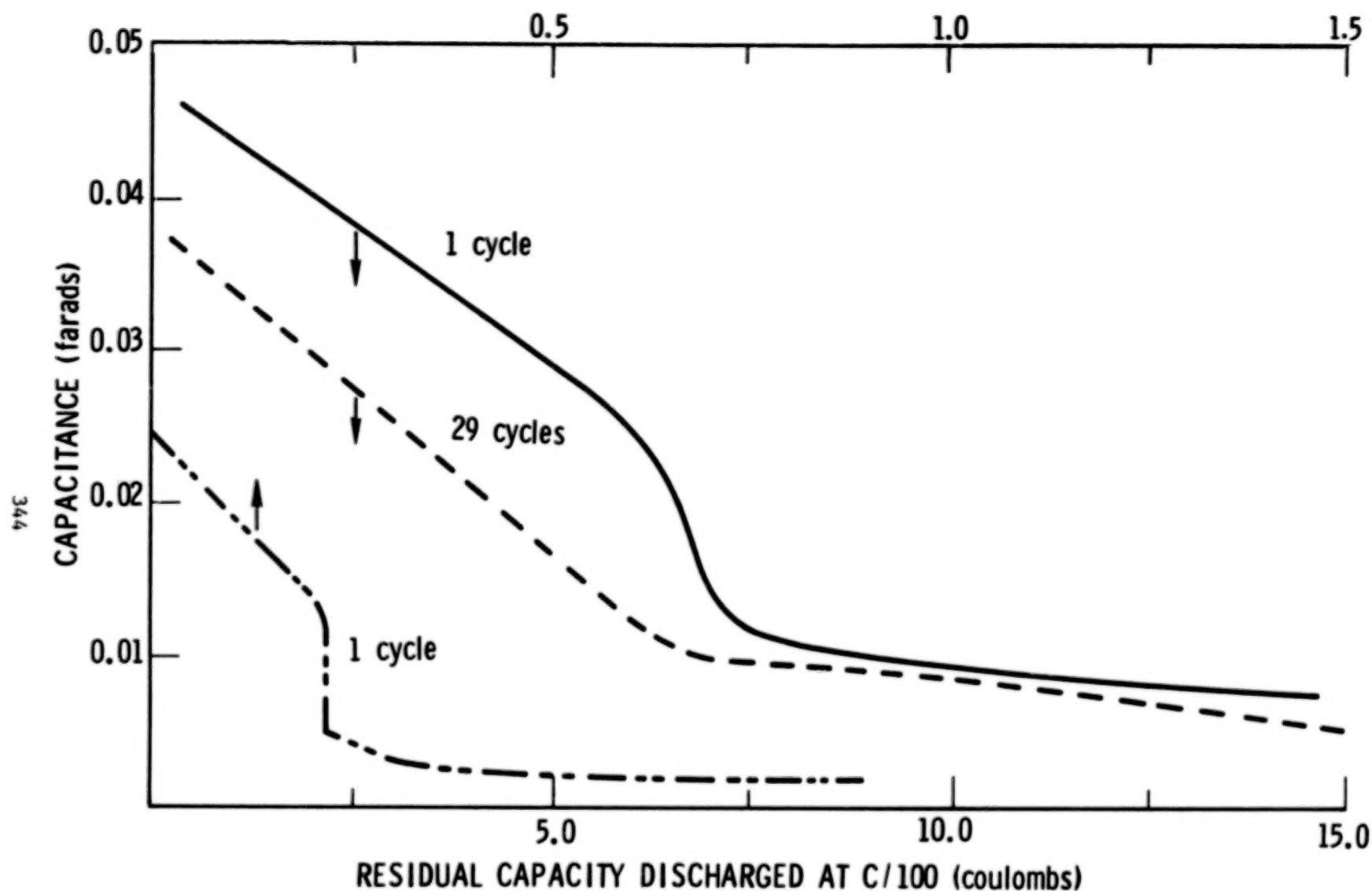
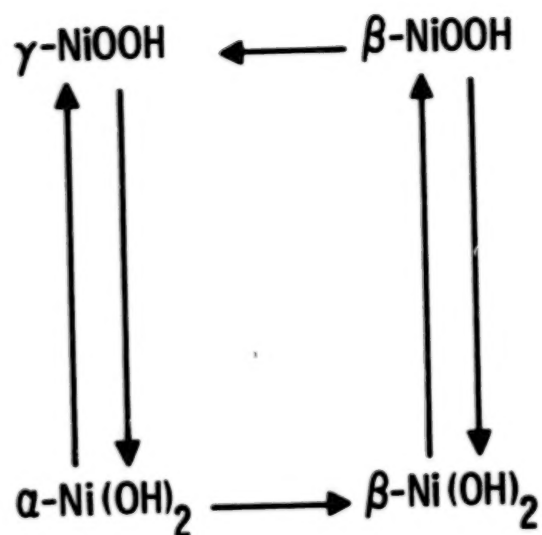
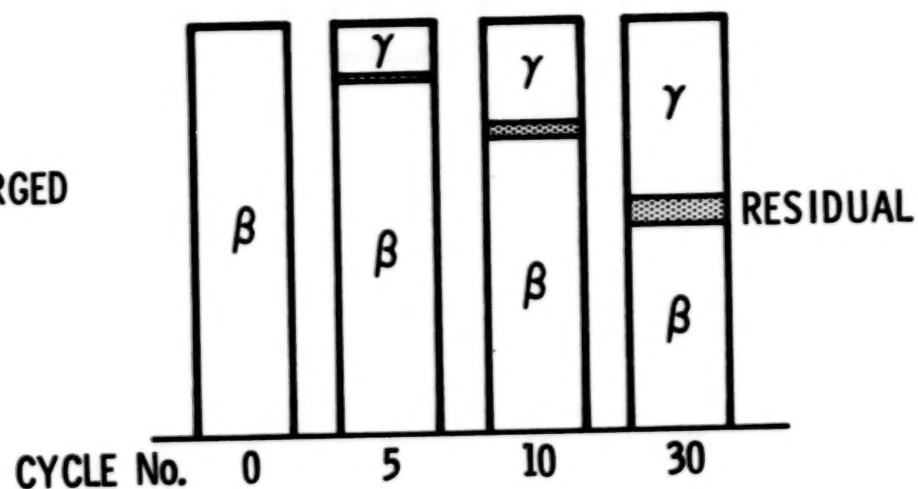


Figure 11. Capacitance of a nickel electrode in the residual capacity region of Figure 9 (C/100 region). Solid and dashed lines are for a sintered electrode and the dot-dashed line is for a flat plate electrode.

344



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DISCHARGED

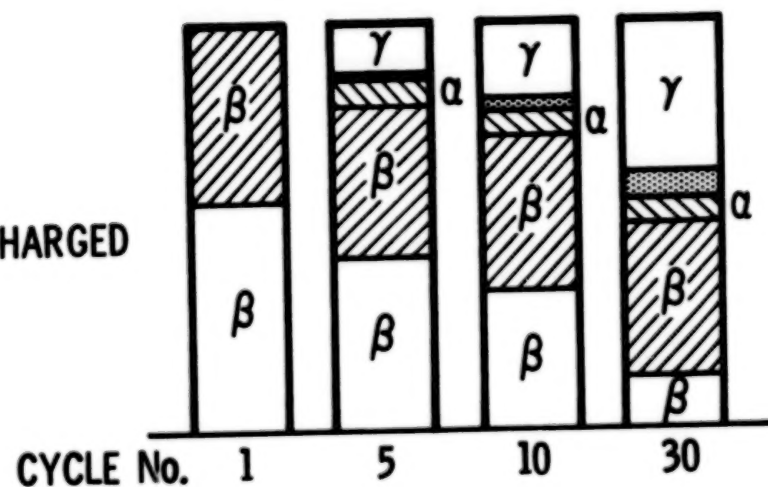


Figure 12. Proposed mechanism for the cyclic behavior and effects of reconditioning on a nickel electrode.

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345

OTHER PRESENTATIONS

STATUS OF SAFT SILVER HYDROGEN CELL DEVELOPMENT

Dr. B. Jacques Goualard and P. Fougere
Aerospace Department/SAFT

**STATUS OF SAFT
SILVER HYDROGEN CELL DEVELOPMENT
NASA BATTERY WORKSHOP 1982**

**Dr. B. Jacques Goualard/Fougere
SAFT
Aerospace Department
Romainville, France**

INTRODUCTION

Theoretical Aspects

Summary of R-D contracts

- Separators
- Positive electrode structure
- Hydrogen electrode
- Stack design
- Hydrides
- Container
- Cycle life tests

Application to hardware

- 26 Ah and 46 Ah cells
- 90 Ah CPV Battery with hydrides

INTRODUCTION

The tremendous growth of the space business over the past 10 years has led to an increase of the secondary power needed on-board spacecraft to power the vehicle itself and the increasing energy requirements of the payloads.

Ni-Cd batteries have been used extensively and have demonstrated their performance in space. The weight penalty that results from their low energy density has prompted the study, design, and development of more efficient couples.

Nickel-hydrogen cells appear to be an improvement over the nickel-cadmium in applications requiring longer lifetime and reduced weight. An even more efficient couple, the silver-hydrogen couple, is also considered.

After a theoretical study first performed by the Battelle Institute of Geneva under ESA (European Space Agency) contract, SAFT has undertaken more detailed analyses of the silver-hydrogen degradation mechanisms. ESA and the French Department of Defense contracted with SAFT for a full-development program of the silver-hydrogen technology.

This program started in 1976 and covered all mechanical and electrochemical aspects:

- Positive, Silver Electrode
- Negative, Hydrogen Electrode
- Separator Material
- Pressure Vessel

More recently, the French Department of Defense decided to evaluate improvements that could be obtained from the use of hydrides within the Silver Hydrogen system and from the use of the C.P.V. concept.

All this development work has been conducted in parallel with the development of the Nickel-Hydrogen system, more specially the pressure vessel, and production of cells exhibiting characteristics in agreement with space requirements is now possible.

THEORETICAL ASPECTS

I will present the work that has been completed: life cycle test results representing more than four years real time and a common pressure vessel prototype battery that was built for the French Air Force.

The theoretical energy density of several electrochemical couples that are of interest for space application is shown in Slide 1.

The theoretical values have been known for a long time and the practical values achieved with nickel-hydrogen and silver-hydrogen systems could provide satisfactory answers to the increasing need for improved energy density.

SUMMARY OF R AND D CONTRACTS

I would like to summarize the Research and Development contracts implemented at SAFT.

SEPARATOR

Separator is required:

- To provide electrical insulation between the electrodes
- To create a barrier against silver ion migration
- To act as an electrolyte reservoir
- To have high mechanical strength and be chemically inert

This list could be extended, but these are the main points.

Unfortunately, no product has all these properties and the solutions generally proposed for cells using silver electrodes consist of an association of two materials:

- Felt as spacing device and electrolyte reservoir
- Membranes as barrier against silver migration

Among the products subjected to preliminary evaluation, four have been studied in detail:

- Polyamid felt (from Pellon)
- Asbestos
- Cellophane C.19
- Polypropylene, celgard 3401
- Stacks of electrodes with these separators associated in different ways have been tested in boiler plates and cells of actual capacity of about 20 Ah
- Electrical testing consisted of characterization at several charge and discharge rates and minimum of 200 to 400 geosynchronous simulation cycles at 50% DOD
- After cycling the destructive physical analysis including specifically determination of the amount of electrolyte and silver in the different layers of separators shows that migration is restricted in the second layer of separator. This is clearly apparent on Slide 2.

The selected separators are:

- Several layers of nylon felt near the positive electrode to provide a good electrolyte reservoir
- Several layers of pretreated cellophane acting as a barrier against silver migration

At The Positive Electrode

The structure changes of the silver grains during cycling is a disadvantage of silver cells. This topic has been extensively studied more specifically with regard to the following parameters:

- Porosity - thickness
- Additives, for example Ni or carbon powders
- Collector grid
- Silver grain size
- Sintering conditions
- Manufacturing process, for example: rolling, compression, slurry
- Electrolyte concentration

A first phase has consisted of potentiodynamic-scanning tests. In a second phase several stack assemblies have been electrically tested in boiler plates under conditions similar to that of the separator study.

Results of the electrical tests, destructive physical analysis and silver plate SEM examination have allowed us to select the most suitable electrode design to cover a wide range of applications.

This standard electrode has the following characteristics:

- Rolling by a continuous process as practiced for many years by SAFT for silver-zinc cells
- Thickness - 0.57 mm
- Porosity - 60%
- Collector: expanded silver grid

Nevertheless, specific electrodes could be manufactured to meet special requirements. For example, thickness from 0.3 to 2.2 mm.

Hydrogen Electrode

A first hydrogen electrode was designed by SAFT in 1974 during the development of the Nickel-Hydrogen system. This electrode was basically the same as those designed previously for the fuel cells.

This electrode has now demonstrated more than 500,000 cell hours of cycling without failure.

More recently, taking into account the development of metal gas cells, an improvement program has been initiated by the European Space Agency in order to:

- Reduce the weight of the electrode
- Evaluate a more economical manufacturing process

The hydrogen-electrode comprises:

- An expanded Nickel grid as current collector
- A porous layer of active charcoal with 5% platinum as catalyst bonded with teflon
- An hydrophobic porous teflon sheet deposited on the gas side to avoid flooding of the electrode

The results of this study are such that the weight has been reduced from 80 to 57 mg/cm², and the manufacturing time reduced by a factor of 3.

About The Stack Design

Several types of stacks have been tested for positive and negative electrodes combinations:

- Single or double plates
- Various dimensions
- Cylindrical and prismatic stacks

The cylindrical selected design consists of:

- Double hydrogen electrodes, back to back assembly

Projections are deposited on the hydrophobic side in order to maintain an electrode spacing of 0.5 mm:

- Single positive electrode whose diameter is smaller than that of the negative one

This configuration allows rapid recombination of oxygen at the end of charge and gives a margin for the shape modifications of the positive silver electrode after long cycling.

The prismatic stack design has proven to be inefficient.

Hydrides

Use of hydrides enables the development of metal gas cells or batteries with considerable reduction of operating pressure and cell volume. For some specific applications where high volumetric energy density is required, it could be profitable to use hydrides at the expense of a small loss of gravimetric energy density.

Hydrides have been selected on the following basis:

- Ability to be used in KOH environment
- Pressure at the hydride plateau
- High hydrogen absorption capacity

Absorption isotherms are presented on Slide 3.

La Ni 4.7 has a very flat absorption plateau, but a low desorption pressure. More extended tests have determined hydride stability, absorption capability kinetics of absorption-desorption, which is a very important parameter for high discharge rates.

Slide 4 shows the allowable charge and discharge current for two selected hydrides.

Cycle life has been tested in Ag H₂ cells with comparison to a reference sample cell without hydride. Test conditions are given in the following slide (5).

On Slide 6 you can see the end of charge pressure evolution during cycling. 3,000 cycles have been accumulated to date and the cycling is continuing satisfactorily, EOC pressure having increased slightly from cycle 2,500.

A full scale Silver Hydrogen common pressure vessel battery with hydrides has been constructed and successfully tested.

Detailed presentation was given last September at the Brighton Power Sources Symposium.

THE CONTAINER has the same design for both Ni-H₂ and silver-hydrogen cells. Until mid-82, the container consisted of 3 parts made out of Inconel 625.

A new container consisting of two parts made out of Inconel 718 has been developed and allows an increase of the maximum operating pressure, consequently improving volumetric energy density.

This container is now in use for cell assembly.

Cycle Life Tests

I will now present cycling test results.

During the last five years, more than 150 test cells (Boiler plates) and 50 cells have been assembled.

Most of them have been analysed after electrical evaluation testing performed during implementation of the R. and D. contracts.

Some have been placed in life cycle simulation in various conditions which are summarized together with results on slide 7.

As it is shown in this table, 18,000 cycles have been accumulated with a DOD of 28%.

The test was discontinued due to failure of the test equipment. This represents more than three years of LEO application performed over a period of four years including activation time and rest due to equipment maintenance.

Results obtained with longer cycles, 6, 12, or 24 hours demonstrate the ability of the silver-hydrogen cells to be extensively cycled, but the number of cycles accumulated to date does not yet demonstrate long mission life of from 7 to 10 years.

At the present time, 46 Ah cells are undergoing geosynchronous simulation cycles at TRW and have successfully completed the first eclipse season.

Application To Hardware

I will now present the application to hardware.

R and D contract cells have been manufactured and delivered to customers for evaluation.

- Typical electrical characteristics are given on Slide 8 for charge, and on Slide 9 for discharge.

The typical voltage plateau is from 1.12 to 1.15 volts.

- General characteristics of silver-hydrogen cells with rated capacities of 26 and 46 Ah are given on Slide 10.

Energy density in the range of from 65 to 80 Wh/kg is now obtained. A maximum operating pressure of 70 bars is now considered with the use of Inconel 718 and will result in an improvement of the cell volumetric energy density.

Comparison between several types of batteries now available or under design is presented on Slide 11.

Batteries in the range of from 1,000 to 1,900 watt-hours at 100% DOD have been selected for this comparison.

- Ni-Cd ECS-2 battery manufactured for ESA and dedicated to the European Communication Spacecraft
- Projected 40 Ah Ni-Cd battery of similar design
- Ni-H₂ Intelsat V battery based on available data from existing literature
- Ni-H₂ battery under design by SAFT for CNES and dedicated to the next generation of Telecom platform A.T.E.
- Projected Ag-H₂ batteries with 26 Ah or 46 Ah as presented on the previous slide

Energy density is:

30 Wh/kg in Ni-Cd
40 Wh/kg in Ni-H₂
50 to 60 Wh/kg in Ag-H₂

90 AH CPV Battery With Hydrides

A CPV Ag-H₂ battery utilizing the hydride technology has been built, and is shown on Slide 12.

This battery comprises several pressure vessels series connected within a rigid structure which is designed to withstand mechanical environments likely to be found in aeronautic applications.

These pressure vessels contain either electrochemical stacks or provide hydride packaging.

In the battery shown, each electrochemical pressure vessel contains three silver-hydrogen stacks with a rated capacity of approximately 90 Ah. These stacks are shown on Slide 13.

You can see the bus-bar which allows the 500 A discharge current required by the specification.

The hydride pressure vessel contains the hydrides. Together with the electrochemical ones to which they are series connected by pipes, they provide volume for hydrogen storage.

- General characteristics of the battery are shown on Slide 14.

With an actual capacity of 90 Ah at an average voltage of 20 volts, the mass is 30 kg corresponding to 60 Wh/kg.

Battery weight breakdown is presented on Slide 15. The hydride selected for this battery provides higher discharge current than La-Ni_{4,7}.

Hydride quantity corresponds to approximately 430 liters of hydrogen which is equal to 40 Ah or 40% of the total battery capacity.

Electrical characteristics are given on Slide 16.

Now, my conclusions.

Five years of extensive research and development activities have led to the manufacturing of practical silver-hydrogen cells.

Life capability has been demonstrated, in particular 18,000 cycles at 28% DOD in LEO conditions have been accumulated.

The energy density of the cells is in the range of from 65 to 80 Wh/kg.

Batteries of these cells have an energy density of from 50 to 60 Wh/kg which represent an attractive mass saving for spacecraft.

Thank you.

SPECIFIC ENERGY OF ELECTROCHEMICAL SYSTEMS
USABLE FOR SPACE APPLICATIONS

SYSTEM	GRAVIMETRIC ENERGY DENSITY		VOLUMETRIC ENERGY DENSITY	
	WH/KG		WH/DM ³	
	THEORETICAL	PRACTICAL	THEORETICAL	PRACTICAL
Ni-Cd	210	30 - 35	730	100
Ag-Zn	440	90 - 120	2150	260
Ag-Cd	270	40 - 60	1400	120
Ni-H ₂	380	45 - 55	1350	≈ 40*
Ag-H ₂	550	70 - 80	2500	≈ 50*

Figure 1

* OPERATING PRESSURE 40 BARS.

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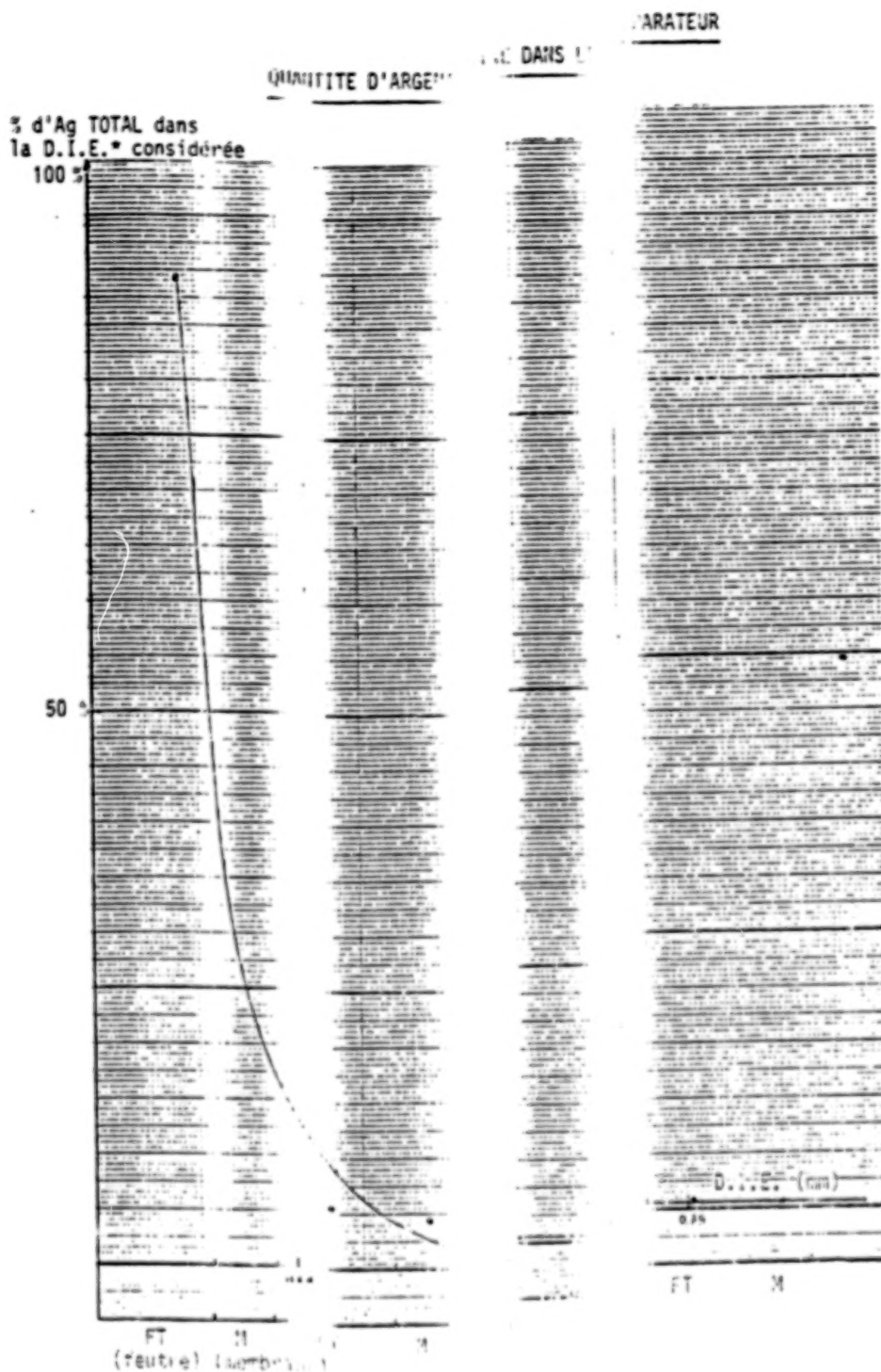


Figure 2

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ABSORPTION ISOTHERMS AT 20°C FOR SELECTED
HYDRIDES

SAS-1025/82-

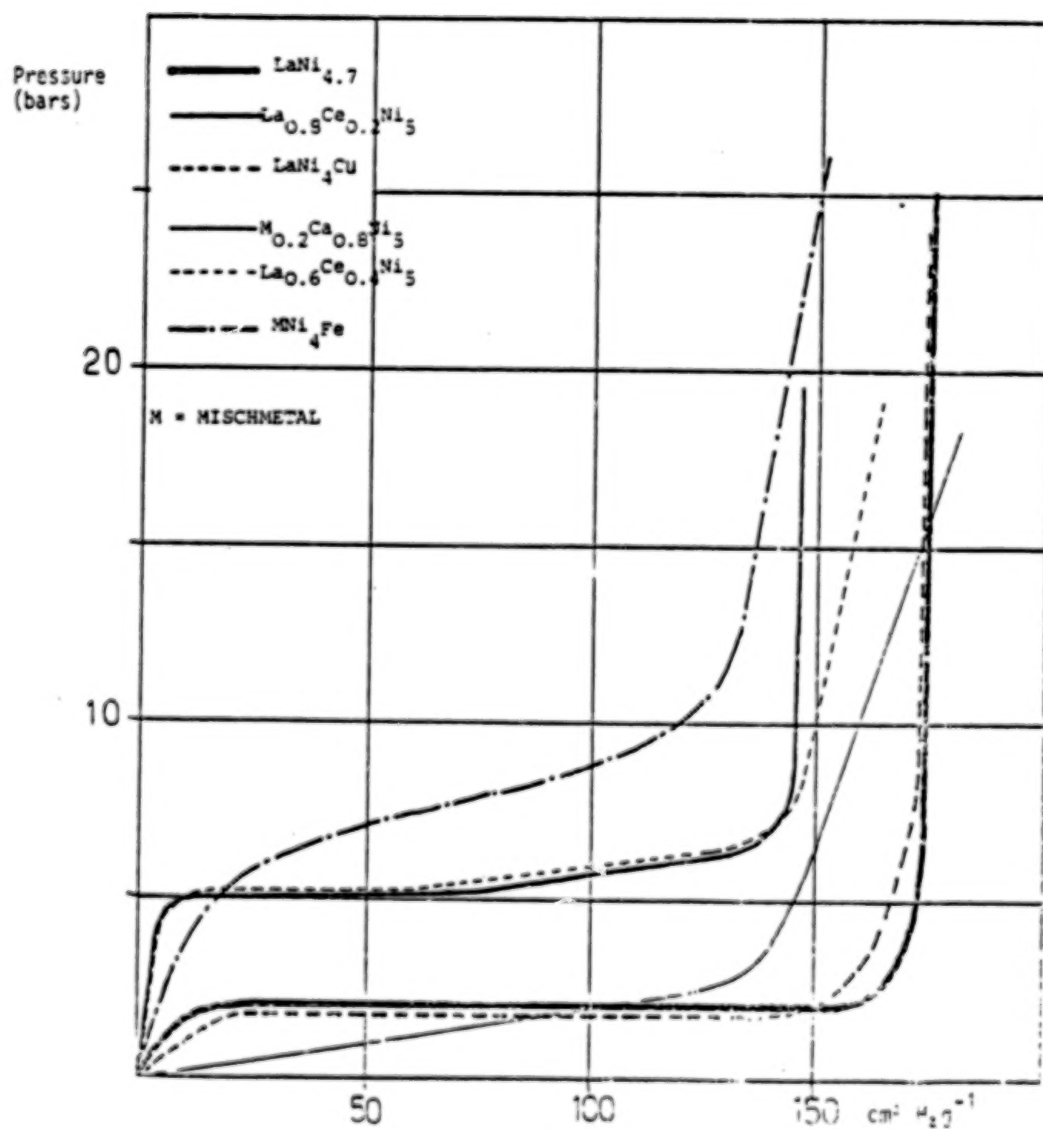


Figure 3

ALLOWABLE CHARGE AND DISCHARGE CURRENTS FOR
HYDRIDE Ag-H₂ SYSTEM AT 20°C

SAS-1025/82

Hydride	LaNi _{4.7}	La _{0.8} Ce _{0.2} Ni ₅
Allowable charge current (mA g ⁻¹)	< 250	< 250
Allowable discharge current (mA g ⁻¹)	≤ 150	≤ 250

Figure 4

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CYCLE LIFE TEST CONDITIONS

SAS-1025/62

TEMPERATURE $20 \pm 2^\circ\text{C}$

Charge rate		Charge duration (hours)	Discharge rate		Discharge duration (hours)	depth of discharge (% C_S) *	Charge coefficient
A	mA/g of $\text{LaNi}_{4.7}$		A	mA/g of $\text{LaNi}_{4.7}$			
0.82 (C/10)	≈ 21	5.25	3.1 (C/2.5)	≈ 78	1.2	≈ 50	≈ 1.16

Figure 5

* $C_S = 7.5\text{Ah}$ = actual capacity of silver hydrogen stack

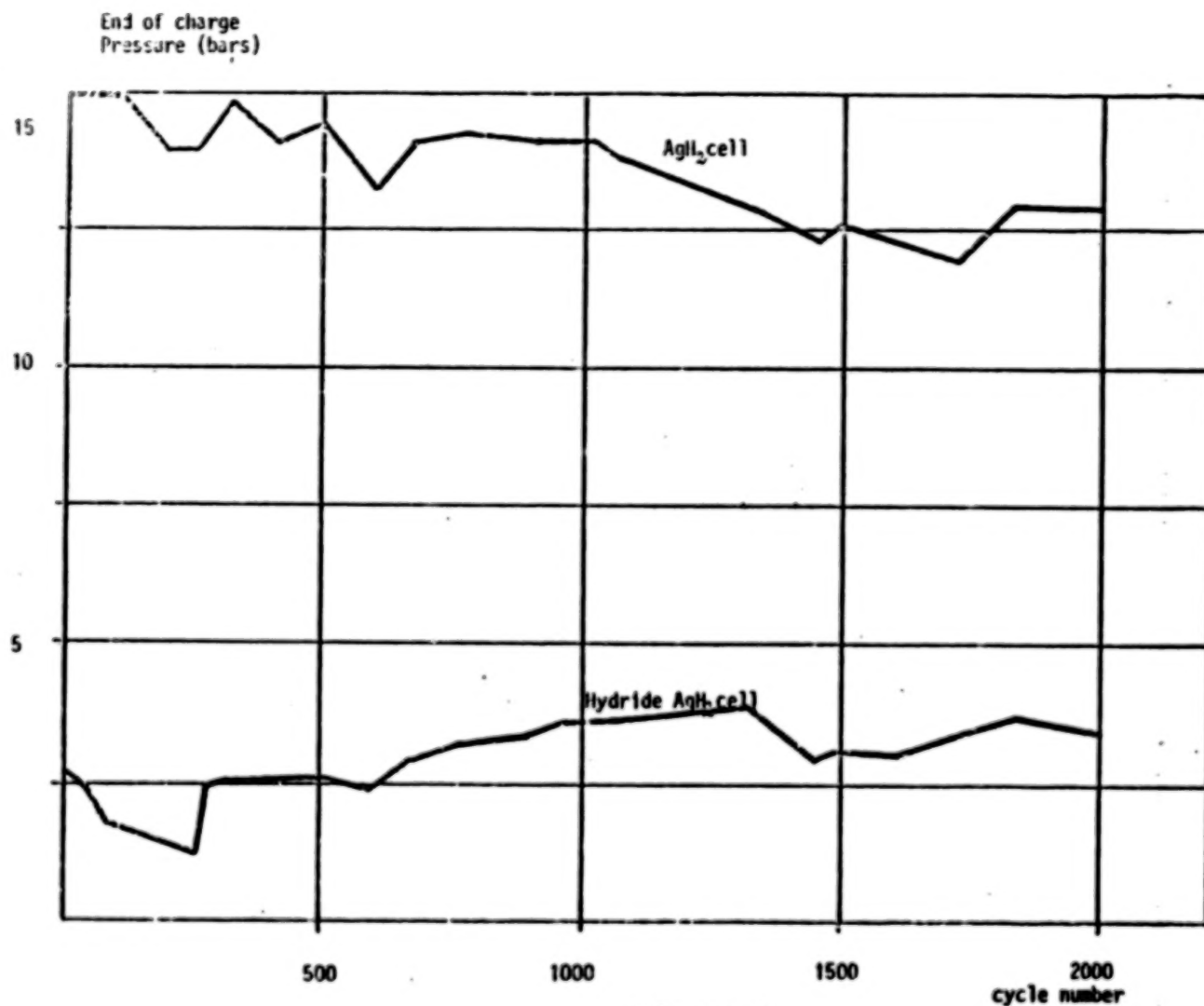


Figure 6

HYDRIDE Ag-H₂ CELL
PRESSURE EVOLUTION DURING CYCLE LIFE TEST

SAS-1025/82-

361

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ACTUAL CAPACITY (Ah)	NUMBER OF CELLS	CYCLE TYPE-DURATION	TEMPERATURE (°C)	DISCHARGE DOD (%)	CHARGE INTENSITY (A)	CHARGE DURATION (H, MN)	DISCHARGE INTENSITY (A)	DISCHARGE DURATION (H, MN)	RESULTS AND REMARKS
24	6	GED-24 H	20	60	0.7	22 H	6.0	2 H	560 _c VARIOUS DESIGN DISCONTINUED
24	3	GED-24 H	0	60	0.7	22 H	6.0	2 H	720 _c VARIOUS DESIGN DISCONTINUED
24	1	LED-100 MN	20	28	5.5	65 MN	9.6	35 MN	18000 _c TEST EQUIPMENT FAILURE. CELLS TO BE ANALYSED
20	9	12 H	20	58	5.8	2 H	1.0	10 H	1500 _c DISCONTINUED
8	6	6.4 H	20	46	0.82	5.25 H	3.1	1.2 H	3100 _c HYDRIDES
8	1	6.4 H	20	46	0.82	5.25 H	3.1	1.2 H	3100 _c REFERENCE CELL
60	4	GED-24 H	5					1.2 H	TRW

CYCLE LIFE TESTS PERFORMED ON AG-12 CELLS

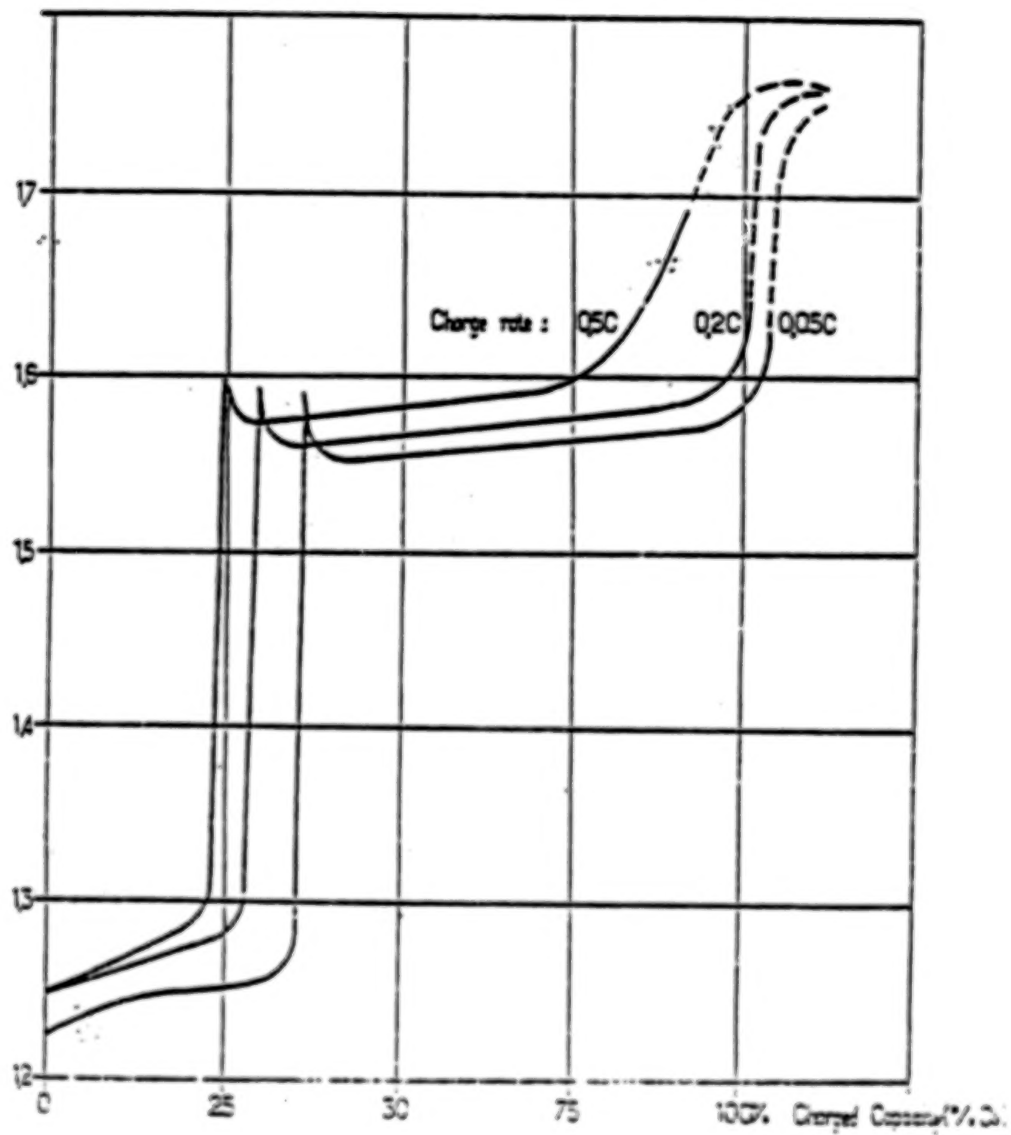
Figure 7

368

SAFT Ag H₂ CELLS

CHARGE VOLTAGE CHARACTERISTICS

Voltage (V)



Temperature: 20°C

Figure 8

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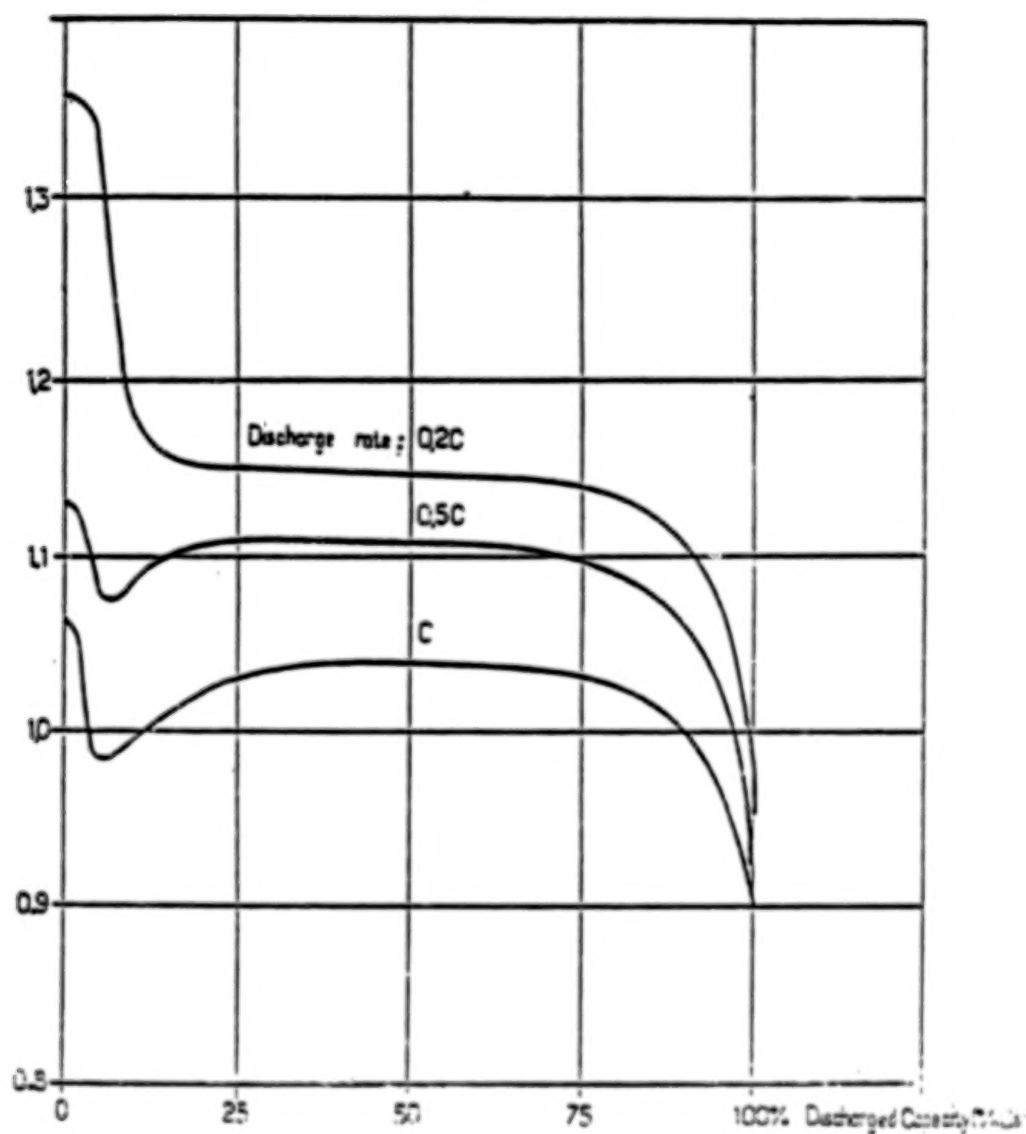
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SAFT Ag H₂ CELLS

DISCHARGE VOLTAGE CHARACTERISTICS

Voltage (V)

After charge at 0.05C



Temperature: 20°C

Figure 9

DETAILED CHARACTERISTICS OF SAFT AG-H₂ CELLS

TYPE RATED CAPACITY	HRA 25 25 AH	HRA 46 46 AH
<u>STACK</u>		
- POSITIVE PLATES THICKNESS MM	8 0.57	14 0.57
- NEGATIVE PLATES PLATINUM THICKNESS MM	16 5 % 0.40	28 5 % 0.40
- SEPARATOR : 5 LAYERS NYLON FELT 4 LAYERS CELLOPHANE	X	X
- ELECTROLYTE : KOH 10.3 N (G)	127	190
<u>CONTAINER</u>		
- INCONEL	X	X
- OPERATING PRESSURE MAX	40 b	40 b
<u>ACTUAL CAPACITY 23°C</u>		
- CHARGE C/20		
- DISCHARGE C/5	34 AH	60 AH
- DISCHARGE C/2	33 AH	
AVERAGE VOLTAGE :		
- DISCHARGE C/5	1.17 V	1.17 V
- DISCHARGE C/2	1.13 V	
INTERNAL RESISTANCE	≈ 5 mΩ	≈ 5 mΩ
<u>DIMENSIONS</u>		
- OVERALL HEIGHT (MM)	177	256
- DIAMETER (MM)	81	81
- WEIGHT (G)	580	880 ± 5
<u>ENERGY DENSITY</u>		
- GRAVIMETRIC (WH/KG)	54 - 56	79
- VOLUMETRIC (WH/LM ³)	41	50

Figure 10

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CELL TYPE	RATED CAPACITY	ACTUAL CAPACITY	NUMBER OF CELLS	AVERAGE DISCHARGE VOLTAGE (C/2)	MASS (KG)		GRAVIMETRIC ENERGY DENSITY (WH/KG)	
					CELL	BATTERY	CELL	BATTERY
NI-CD ECS-2 SAFT	24	28.5	32	1.20	1.00	35.05	34.2	31
NI-CD HIGH CAPACITY SAFT	40	48	28	1.20	1.59	49	36.2	33
NI-H2 INGELSAT-V	30	35	27	1.20	0.89	30.15	47.2	38
NI-H2 SAFT	30	36	28	1.25	0.95	32.5	48	39
AG-H2 SAFT	26	33	28	1.13	0.58	20.3	64.3	51.4
	46	60	28	1.13	0.88	30.8	77	61.5

Figure 11
COMPARISON OF NI-CD - NI-H2 - AG-H2
BATTERY PERFORMANCES

366

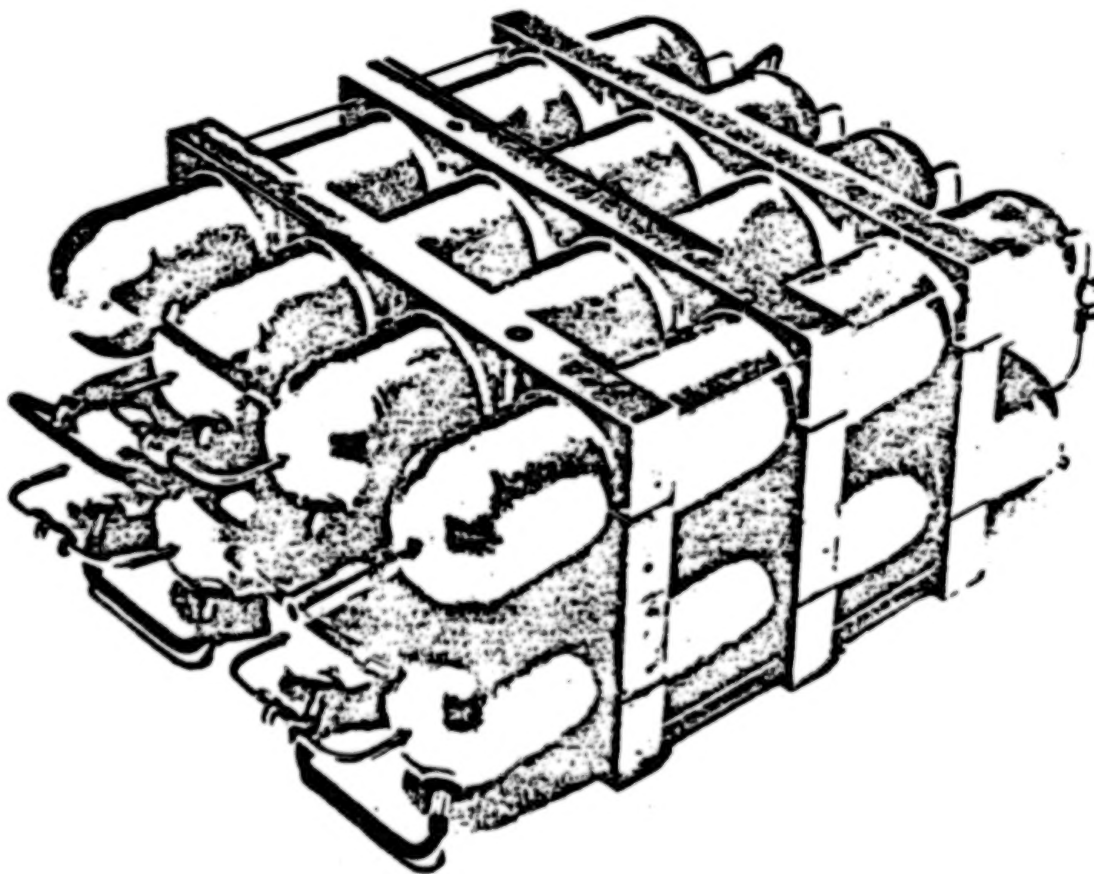


Figure 12

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FINAL SILVER HYDROGEN BATTERY STACK ASSEMBLIES

SAS-1025/82

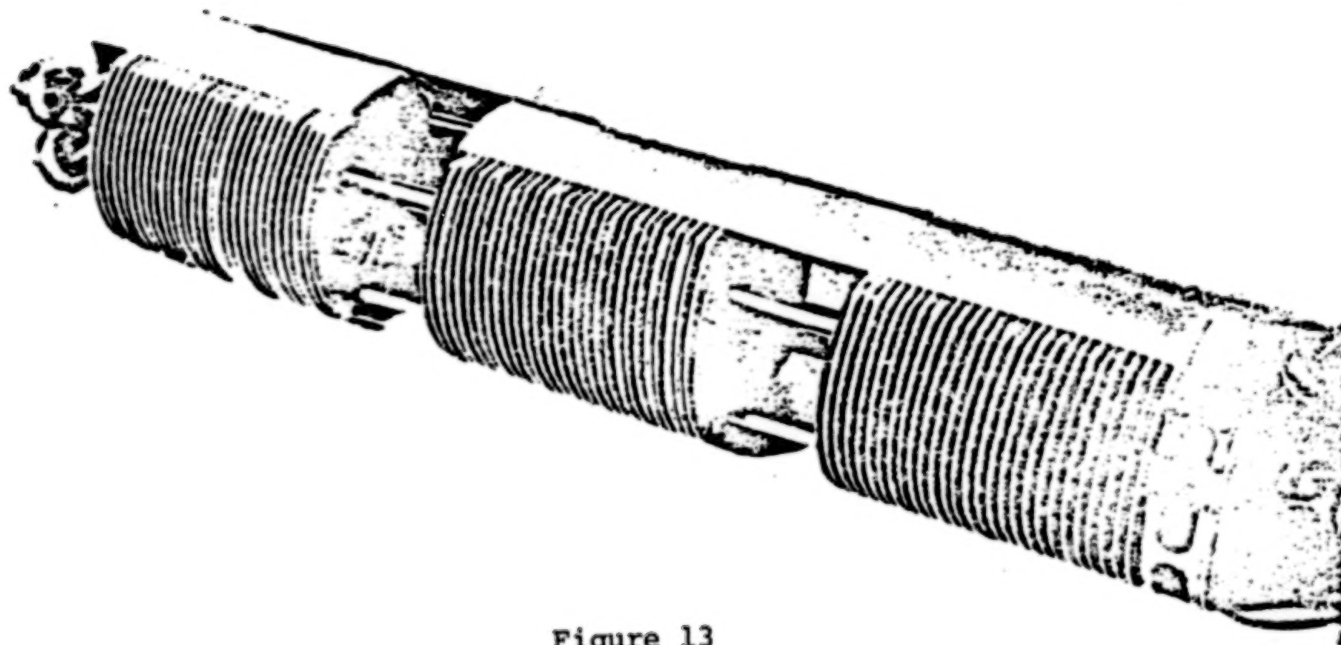


Figure 13

368

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TABLE 14

HYDRIDE Ag-H₂ BATTERY CHARACTERISTICS

SAS-1025/82

Actual capacity (Ah)	90
Voltage rate during discharge C/2 rate (150A)	19.8
Maximum operating pressure (bars)	40
Overall length (mm)	500
Overall width (mm)	400
Overall Height (mm)	200
Height	30.0
Energy density (Wh/kg)	≈60
Specific energy (Wh/dm ³)	≈45

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WEIGHT BREAKDOWN OF HYDRIDE SILVER HYDROGEN BATTERY

SAS-1029/82-

Component	Weight (kg)	%
Silver hydrogen stacks	9.12	30.5
Electrolyte	4.68	15.6
Pressure vessels + pipes + terminals	4.43	14.8
Hydride vessel	0.30	1.0
Hardware + external Connections	4.36	14.6
Structure	3.41	11.4
Hydride $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$	3.61	12.1
TOTAL	30.0	100

Figure 15

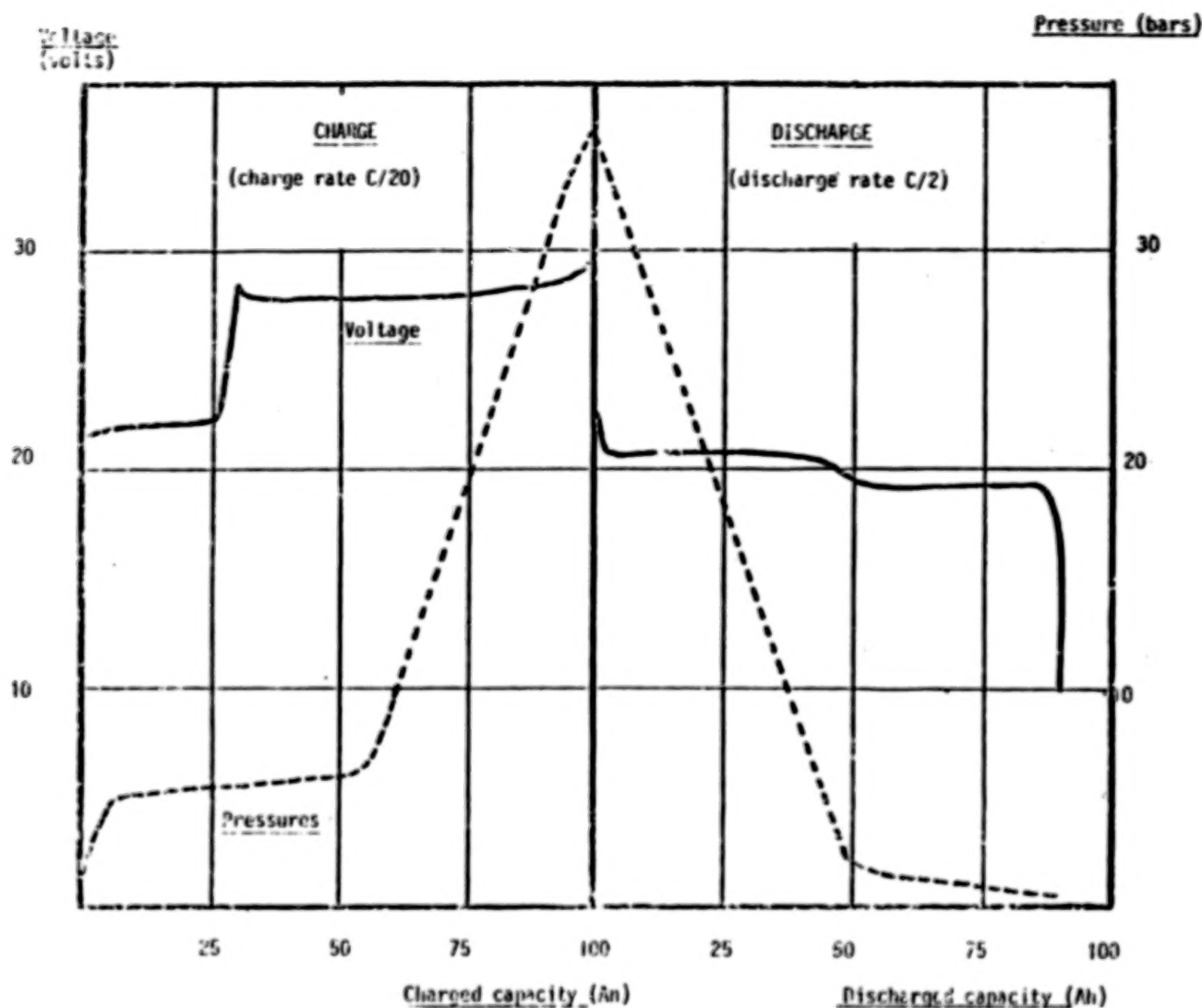


Figure 16

SESSION IV

DISCUSSION

- Q. Weiner, Aerospace: Other than measurement of reconditioning how can you determine accurately what the actual depth of discharge is? Isn't voltage the most sensitive parameter at that point?
- A. Scott, TRW: Voltage is very sensitive but not to depth of discharge. It's much more sensitive to current and to the exact condition of the cells.
- Q. Weiner, Aerospace: Once you are able to get the battery to discharge, let's say to even 100% of it's rate capacity, and of course preferably actual capacity. Each time you repeat the process it is a little easier to keep the voltages from coming down.
- Q. Unidentified: Might not all these repeated discharges actually end up shortening the life of the battery?
- A. Weiner, Aerospace: I see no evidence of that.
- Q. Ritterman, TRW: I don't have any data for actual spaceflight qualities of nickel-cadmium cells but I have built some laboratory cells. This work I did for NASA and there the opposite effect took place. That is to say it would seem that the cells, the recombination rate, decreased with the age of the cell, and that would be equivalent to the pressure increasing with the age of the cell. There may be some data contrary to that in actual flight or lab tests experiments, but that which I did observe with the cells, I built.
- Q. Milden, Aerospace: On the basis of the Kren testing it appears that because of their natural reconditioning that it's well worth reconditioning on lower orbit type regime. Gerry presented a paper at the IUC showing that you could get on a 25% depth of discharge maybe 3,500 to 4,000 cycles before you reached under

voltage and if you did deep discharges and reconditioning you could go 12, 15, 20 thousand cycles even though with orbit type regimes. So it might be valuable on lower earth orbit. It's still to be proven.

- A. Van Ommering, Ford: I just think there's not enough data available on it. One of the problems is again you might, in a certain situation, be dealing with a cell design that has a problem to begin with, say lower electrolyte reconditioning might help you more. So it really has to be studied more systematically before anyone would go ahead and do that.

COMMENT

- Q. Berry, Aerospace: In regard to the lower earth orbit reconditioning, I recall at the workshop five years ago that there was a session devoted to battery experience in lower earth orbit in which Gerry Halpert alluded to earlier. It was remarkable that every one of the lower earth orbit spacecraft had found it necessary or highly desirable to accomplish reconditioning indirectly even though they weren't designed for it.

COMMENT

Gross, Boeing: We ran some comparative tests in lower earth orbit with and without reconditioning and found that reconditioning is helpful for the lower earth orbit case. We used these results about five years ago in the Battery Workshop.

COMMENT:

Betz, NRL: We, in an attempt to establish whether the deep reconditioning would work in near earth orbit, have been attempting to run some tests like this for the past two years or so. Unfortunately I don't have any data with me and some of the results are fairly recent. It simulates a near earth orbit very much like Gerry's orbit was described this morning. There are periods of 100% seen where one has the opportunity to take a battery off line and recondition it. The tests I did accelerate somewhat instead of using the 55 day 100% seen periods that one might see in the orbits that I had an interest in. I doubled the depth of discharge to about 40% depth and reduced the reconditioning period to sometimes 25 days, sometimes 50 days, sometimes 75 days,

which kind of maxed the type of orbit I could see the satellite might have. Over the period of time, I think to ten thousand cycles, we had about ten or 11 reconditionings that we would cut at 300 to 600 or 700 cycles. Initially the end of discharge voltage was always substantially, oh-- incidently I had a control group. The control group was cycled in the same circuit, but during the reconditioning period was trickle charged at the C over 60 rate while the other battery was going through reconditioning. One might mention that the reconditioning we used was roughly at the initial cover 120 rate and we did allow all cells but one to reverse. The current of time that the load resistor was on the five cell battery could be as long as 300 hours or what, like ten to 15 days. The final current, when everything came together, was roughly two milliamps on a six ampere hour battery. As indicated, the voltage performance on discharge for the reconditioned battery consistency looked better, but there was still a trend that you could see that the battery was showing degradation. The end of discharge voltage was not recovering as high and was going lower with each subsequent reconditioning. The second thing that we noticed was that the end of charge voltages on the reconditioned battery pack were somewhat more variable than those that were being trickle charged over the period instead of being reconditioned. And the final results, more recently in the ten thousand cycle region, is that three of the five reconditioned cells have failed by shorting and all of the five cells in the trickle charge mode are continuing on cycling with end of discharge voltage roughly 1.08 volts per cell.

- Q. Ford, Aerospace: You showed a couple of graphs on your analysis to the Kren data. In the two different capacity measurements you showed linear curve, or linear decline in voltage, from the one capacity measurement to the next one. I think that the other gentleman was really asking the same question. Was that really a linear declining voltage or was there a very rapid initial decline aspect?
- A. Gaston, RCA: I don't have all the cycles and I have looked at only specific cycles. So when you say linear decline from cycle to cycle, I don't have that. I cannot answer whether it was a gradual function or a distinct function.
- Q. Birken, Aerospace: Chuck, did you say that there was a difference in reconditioning effect that was dependent on the charge rates?

- A. Badcock, Aerospace: In all the parameters that we did in the cells, the only thing that really was dramatic in effect of voltage depression was on charge rate, depth of discharge and discharge rates. But the charge rate did lower the moment it was observed per cycle.
- Q. Gross, Boeing: Chuck, you had concluded that reconditioning at low rates is superior to reconditioning at high rates. This appears to be based on the test where you discharge to 1.1 volts per cell at varying rates but the discharges at the high rate would reach that point at a lower amount of removed capacity than discharge of the lower rates, therefore; you are seeing in effect the extent of discharge rather than the rate itself.
- A. Badcock, Aerospace: Yes, that's true. Clearly, one of the reasons you recondition at a low rate is because - well, as indicated - you wish to turn over all the active material and you need to go to a low rate to do that unless you want to reverse the cell at cover two, which is not a good idea - we tried that.
- Q. Lim, Hughes: Chuck, I'm wondering about your explanations of the high capacity with gamma and beta. I understand the gamma state had a much higher capacity than the beta state. It looks like that after reconditioning, if your explanation is right, it would be contracting to that model. Could you explain?
- A. Badcock, Aerospace: Well, I'm not sure I can. I would make a comment on that. One of the things that puzzled us for quite awhile is when we would see reconditioning data on some spacecraft. The first reconditioning discharge curve would quite often show more atmosphere capacity than the second curve and we ascribe that to gamma phase building up during discharge. That's what we ascribe it to.

COMMENT:

Halpert, GSFC: I'll just make the comment that we've seen the voltage degradation on the position that Chuck's alluded to today. We've seen voltage degradation on the megature which Dunlop and some others have alluded to previously. We've been discussing for years whether to use the positive or negative. I think it's both, and as a matter of fact we have some data to show that the second plateau may be due to the negative in some cases but it really depends on the design of the cell and how you are actually using it.

- Q. McDermott, Coppin State: Besides gamma and beta could there also be a difference in crystal size and the contact with the crystal--with the conducting matrix and redistribution of electrolyte? Are there some other possible explanations?
- A. Badcock, Aerospace: Yes. One of the reasons we fell the residual capacity bureaus up in a cell is that you develop a resistor that does not allow an adequate conductivity and there's where the nonconformity actually arises. We think reconditioning helps to make the electrode more uniform.
- Q. Miller, Eagle-Picher: In our work with the silver-hydrogen system we found the water imbalance problem associated with this chemistry to be a very different problem to handle, particularly with the large system it made an 800 ampere hour cell. We found that the water imbalance problem resulted, relative to the operating system in extremely low rates. Practical solutions we found in smaller

cells to accommodate this water change with its cycling resulted in design limitations that really consumed any true volumetric energy density associated with this system. I guess I'd like to ask you if you've overcome this problem or if you could comment on that?

- A. Fougere, SAFT: We say we have studied this point. We don't deny some combination of a number of layers of felt near the positive electron, which provided good flooring for the positive electron. Nevertheless, after doing cycling for elevation of those different stack assemblies, it was clearly seen that reconditioning of the silver-hydrogen cell electron will be more necessary than, for example, nickel-hydrogen. It seems that the behavior is ours for nickel-cadmium. Is this an answer to your question?
- A. Miller, Eagle Picher: I think that will suffice for now. Thank you.
- Q. Gross, Boeing: Could you go a little further into Lee's question--your answer of Lee's question? It's not really clear to me how you solve the problem. You allow the nickel-electrode to flood and the silver-electrode to flood?
- A. Fougere, SAFT: In fact, our design is such that there's a silver layer of nylon felt near the positive. This feeds the positive electrode with a good electrode outlet. So, we have not really identified a electrode management problem; perhaps there is one but we haven't identified it.
- Q. Methlie: Did you have difficulty with the serium hydride alloy reacting with water vapor from the cell itself with time and cycling, and if you did what did you do about it?
- A. Fougere, SAFT: As far as I know, we have not identified that problem. We haven't identified any special problem with the cell.
- Q. Halpert, GSFC: Alright, I'll start it off Chuck. The question was continually raised during your presentation about the different forms of nickel-hydroxide. I believe you alluded to the fact that these were just means of explaining the results that you got, that you actually didn't attempt to measure any of your various stages in the plate. Is that correct? And my question is simply do you have any plans to do that to substantiate your theory?
- A. Badcock, Aerospace: I really doubt that we will right now because we

think that there is some very good evidence in the literature and what we've been trying to do is correlate what happens in a real live cell with what has been published by Bernard and other people.

COMMENT

Unidentified: I have a couple of comments. One is that the identification of beta and gamma transitions that you showed, I believe that the beta or gamma form in the charge state discharges to beta not to alpha as you had it shown on the graph, but the main discharge mode from gamma is back to beta again. Now on charge it goes from charge beta to charge gamma. I think this was reviewed last year in a paper here. The paper showed the effect of aging on the electrochemical and chemical positive electrodes open circuit and shortage storage, and it showed that the loss for capacity in these electrodes was ending up a gamma prime.

My other comment is what you see many times in cells that have been cycled and aged for a long time is that the discharge voltage plateau has a large step at the end. It's something like 100 or 120 millivolts. And this, I think in the past, has been associated with negative electrodes. The step that you were showing, I believe, on your curve is more of the 30 to 40 millivolt range. So part of the conclusion here may be that we are talking about two different animals, two different aging effects. One on the negative cadmium structure and another positive.

- A. Badcock, Aerospace: I'd like to address the second one, I prefer that Albert address the first one, because he was shaking his head when you were commenting on it. There you probably are correct. We were describing just what we saw in a cell and the deltas that we saw over 100 cycles were typically 60 millivolts.
- Q. Unidentified: I'm not familiar with the review that you are talking about, but in going through the literature on this, and from what I've seen in all the papers, the delta and nickel-hydroxide charges to the beta phase, and the alpha nickel-hydroxide phase charges up the gamma phase.
- Q. Gross, Boeing: It is possible, Chuck, that you obtained your nickel-electrodes from a nickel-cadmium cell. If so it would certainly have cadmium in it.
- A. Badcock, Aerospace: Yeah. The one where I showed the effect of the nickel-electrode was giving us the predominant delta V. The cells that we were talking about were nickel-cadmium cells and it wasn't an electrode from a nickel-cadmium cell that we showed with the third electrode. The subsequent studies with the individual

nickel-electrode and on homemade electrodes are pieces that had not seen cadmium. Your point is well taken though. Some of these did have cadmium. We can't identify the effect of cadmium but we think there probably is one.

- Q. McDermott, Coppin State: Is there a possibility that we will eventually have the ability to recondition and know what the effects of reconditioning will be, but that we will not be able to do this at a battery level? We could not do it at a cell level recognizing individual cell differences. Would this be coupled with an individual charge control microprocessor and so on? We need a reliable system where in effect you could eliminate some of the fears of cell reversal if you could simply be able to control each cell in the battery. Is this going to come?
- A. Badcock, Aerospace: I really wonder if it will not because that implies a great deal of complexity and our questions about reliability associated with that complexity may or may not be necessary. The problems of individual cell control are really ones of complexity and expense. I guess the vehicles now have scanners on them and we see individual cell voltage, but I'm not real sure what we are doing with that data yet. Perhaps we can comment on that.

COMMENT

Scott, TRW: Yes, TDRS has a cell voltage scanner on board and the data will be monitored on the ground, but all of the operational nitty-grittys have yet to be worked out as far as exactly what is going to be done with that cell voltage data. But one of the justifications that was involved in putting that scanner on in the first place was just about what we were talking about here; mainly to be able to recondition that battery by deep discharging without having to guess as to what the cell voltages are doing so that if one wished to prevent any cell from reversing doing that process you would have the unambiguous data to do that with. Exactly how that's going to be implemented is yet to be determined.

- Q. Maurer, Bell Labs: I believe the scanners on the TRS only go down to 7/10 of a volt, and in some of the operational plans I've seen they are going to take the battery down to a pretty low voltage. So I can't see where the scanner will be much help for reconditioning.
- A. Scott, TRW: Well you're right, it can't be much good below 7/10 of a volt, but you can do the best you can down to that level, which is a lot better than you can do now as far as anticipating whether one or two cells in the battery may be a lot worse actors than the other, even at 7/10 of a volt.
- Q. Dunlop, Comsat: Gerry, you may want to address questions or comments on this.

Halpert, GSFC: Five spacecrafts did have a scanner, there are what, five of those up now, and the method of reconditionings is to go to when the first cell hits zero to nine volts. We've been using that for about a year and 1/2 now, I guess, and that is the way we expect it to continue to go. We are accomplishing with that basically what Will Scott talks about and that's the intent, to accomplish deep depth of discharge on the battery without getting any individual cells into reversal. On the case of Land-Sat 4 spacecraft, that's an older spacecraft and we have a reconditioning scheme now where we only look at terminal voltage and that's very difficult. We know that we are reversing cells when we try and recondition batteries.

COMMENT

Maurer, Bell Labs: I'd like to get back to the alpha beta gamma transitions again. Alpha nickel-hydroxide is thermodynamically unstable in high concentrations of KOH and will spontaneously arrange to beta form on discharge. You can see this in the potential scans, if you do a potential scan, on a freshly prepared electro-chemical electrode where you start off with alpha you can see the charge peak shift to higher values as you form the beta, and on these transitions where you charge to a potential where you get gamma form, you find the subsequent charge peak is still in the same position. So the gamma has discharged to beta and recharged by beta transition again. So the gamma discharges to beta in a real kind of cell environment where you have high concentrations.

- Q. Dunlop, Comsat: I'll ask the audience a question. We are trying to distinguish here between the effects of the nickel-electrode and the effects of the nickel-cadmium electrode. Perhaps people have some information to contribute on cells, reconditioning of cells. If anybody has some information that might add to the discussion please share it with us.
- A. Scott, TRW: I'll comment in IUE. IUE is not reconditioned at all, no provisions for it either.
- Q. Pickett, Hughes: I know there are a lot of questions about Will Scott's paper that people didn't have an opportunity to ask since I advised the audience not to ask questions other than clarification of papers. I'm sure there were others, and I would like to ask now if there is any one who has a question or would like to make a comment on deep discharge reconditioning to please do so. Do you really need to go to a voltage as low as one volt per battery to effectively recondition the battery?

- A. Maurer, Bell Labs: It is not necessary to go to one volt per battery in order to recondition a battery. If you can work the discharge up at a higher battery voltage. You can do this by starting out very soon before any significant amount of degradation has accumulated, and if you keep at it you can discharge a battery to a very high depth of discharge at a reasonable low rate without the battery ever going below about one volt per cell, which is 20-22-24 volts per battery, if you wish. The point is, the only time you are forced to go to very low battery voltage and reverse cells is if the battery is in such a condition that you have to get there in order to get to a deep enough discharge. Once you get there you can keep the battery in good condition. For example, in orbit right now on the Fleet Sat Com Program the rated capacity there is 24 ampere. For several years now we have been getting 32 ampere hour discharge out of those cells on without ever going below, I believe 8/10's of a volt per cell. We do that by starting in that way and continuing that way throughout the mission so you are not obliged to go down to that low of voltage on the battery.
- A. Ritterman, TRW: On Fleet Sat Com we had a laboratory cycle simulation where we did 95 seasons at 75% DOD at reconditioning down to a battery voltage of close to zero volts. I think the way it was run, and I've shown this viewgraph since 1977 and this year I did not take it along with me. I believe that when we discharge or recondition to one volt per cell we did not get the life that we achieved going down to one volt per battery. I believe that those cells had degraded. So I agree with Will that if you start out early enough and if you use a low enough rate you can achieve the reconditioning at one volt per cell, but once a battery goes sourer you would have to recondition it to the lower voltage.
- A. Halpert, GSFC: I think we need to ask the panel members a question. We've been listening to a lot of, "this is the right way to do it", etc. What I'd like to have each of the panel members do is to tell us what he has actually done in reconditioning, and what I mean by that is tell us how you charged the cells. Give us some information about size, capacity, how you discharge the cells, what the reconditioning procedure is, and tell us if you think it was done the right way, and if it wasn't what you would do differently.

COMMENT

Panel members (unidentified): It's a tradition in this industry that you never do something twice, but on the NATO program we have a system of three batteries normally 20 ampere hours and we do recondition now before every equipped season on those batteries. We haven't always done that in the past but we think it's a good idea. We switch a resistor across each battery which takes the battery down

in a period of 16 hours. That's a relatively fast reconditioning. They are recharged at the sequenced rate of six ampere hours and we recharge them to no more than 130 and put them back on frequency charge. At the end of reconditioning cut off we are basically looking for one volt per cell before we actually achieve a cutoff. On our C-S program we basically run the same kind of battery and we run it the same way, as far as reconditioning is concerned. There we have a constant curve note for recharging, but there is nothing particularly dramatically different. Our experience with those programs is our batteries continue to do very well when used primarily for reconditioning method. So it's not particularly dramatically different. Our experience with those program is our batteries continue to do very well when used primarily for reconditioning capacity. The battery started out at 22 ampere hours, beginning of life, and most are still delivering more than 20 ampere hours with this reconditioning method. So it's not particularly deep but it seems to be working well. And if discharge voltages on both programs are holding up adequately, although the depth of discharge on the NATO program isn't very severe, then things are looking good. On the L-Sat 5 program the discharge is at approximately cover five rate; that's a 34 ampere hour battery 28 cells and the cutoff is based on the first cell reaching .9 volt level where, we recharge the battery. So far as I'm aware the performance in orbit is quite satisfactory.

- Q. Badcock, Aerospace: In practice we are at the present implementing the discharge on all spacecraft that have the record, which is about all of them we are working with right now with the single resistor cast of battery terminals. The size of that resistor per cell has been getting larger as time goes on so as to reduce the rate further in order to help the end of discharge. We're down to somewhere around c/150 at present. Therefore; operationally, we do the reconditioning near the end of each equipped season by going into the discharge directly from the trickle charge. The end of the discharge voltage does vary from program to another, because of various customer requirements. Mainly, we still we recognize that if necessary we can go down to the order of one volt per battery based on our ground test data; some customers won't buy that. For example, in one case is the Fleet Sat Com System where we negotiated with a customer to allow a dual criteria, that is as long as we could obtain a certain capability on that lower discharge, maybe 28 ampere hour, as long as we can get at least that number of ampere hour out on the reconditioning discharge we can stop; or if we reach a point of eight volts per cell before we get there, then we have to stop. So then, as I'll say, I can't recall how we have been able to get something of the order of up to 32 ampere hour out of 8/10 of a volt. On recharge we use whatever the standard recharge current is an charge control that exists in the spacecraft. Nothing special is done, we simply take the battery on to the bus and it goes through with automatic end of charge sequence and goes back on to trickle charge.

A. Panel member, Unidentified: I work for Aerospace and we don't make any spacecrafts we make viewgraphs! I guess I'll make a comment on something Willie said. I think on some vehicles you also leave the battery standing open circuit until it reaches certain voltage so you can maintain control of the system. In general I'll make a comment, that I think adequate reconditioning is the real name of the game here, and you apparently need a very low rate to do that. There are some questions about bringing a deeply discharged battery back on the charge. At say, c/10 rate, you will see some high voltages and I think that's highly overrated as a problem, but it can occur. From a spacecraft design point you want to keep it down, and to do that you want a resistor and you want to use the standard charge control system without putting on anything special just for reconditioning.

Q. Stockel, Comsat: Does anybody actually hardwire a resistor for the cells?

Q. Panel Member: Do you mean to leave it on there all the time?

A. Stockel, Comsat: Yes.

A. Panel Member: We don't, but of course if you want to make it small enough, if you have the time to wait for a very small resistor it probably wouldn't make any difference. You could leave it there all the time and just disconnect it from the load and you'd be off and running.

Someone may worry during continuous trickle charge that we are getting our trickle charge rates down so low that it's going to be putting on a squeeze.

I think Chuck raised an interesting issue and that is what is adequate discharge? From a functional point of view I don't think we really know what the optimum amount of discharge is to do the job. I expect it's a continuous function. You can do as well as you want depending upon how efficiently you discharge the battery. I expect in many cases we are overdoing in terms of the minimum we would have to discharge in order to get satisfactory performance. In a number of our spacecraft we are seeing absolutely no decline in the end of discharge voltage in the middle of the seasons from year to year.

Q. Unidentified: Let me just paint a theoretical picture now getting away from a geo-satellite to a low satellite designed not to require reconditioning. However, after sometime in orbit it develops a problem such that I'm not holding voltage and I want to recondition it and I want your recommendations as to how to do it. First thing I was going to do was discharge the battery perhaps

through a large resistor, as I understand it to be a very low voltage, maybe five volts on a 20 cell battery. The question is what potential gain would I have that instead of putting that battery on a line, I simply charge it up and completely recharge discharge it the second time - gaining capacity and voltage.

- A. Scott, TRW: Well, in general, if you can't for various reasons, do a functionally efficient job in one reconditioning cycle then you can always do better the second time. Another thing is if you are constrained as far as rates and voltages are concerned, then multiple cycles with those constantly comparable do you a lot of good. So you don't unnecessarily have to go flat out unless you have no other options except to get it all done in one cycle, and that's probably rarely the case. Operationally, it's probably easier to do it on one cycle than on several.
- Q. Unidentified: Then if I went flat out being somewhere what, one volt of cell on the whole battery, is that what you mean by flat out?
- A. Scott, TRW: That's what I had in mind.
- Q. Unidentified: Okay if I went flat out you would expect no extra benefits than if I went with another cycle, is that true?
- A. Scott, TRW: Okay - I'm contradicting myself. Let's talk about capacity. If you were able, however; you did it to discharge essentially everything, every bit of theoretical capacity, or close to it, - 80% or more, then no matter what the voltage was I would expect no appreciable additional benefit by a second cycle.
- Q. Dyer, Bell Labs: Will Scott, I'd like to ask you about a comment you made that reconditioning can occur by prolonged overcharging. You restricted your comments to low-earth orbit situations; you also mentioned that this was possibly due to inadequate charging. Could you expand a bit about this kind of reconditioning? Why prolong overcharging? Why not just put in 20% more than theoretical capacity?
- A. Scott, TRW: Well first of all I don't have a lot of information on that type of reconditioning. I was just mentioning it in passing as, ah, to simply contrast that reconditioning procedure with others, depth of discharge for example. But more specifically I believe that there's various data around that suggests that, well practically speaking, you need to keep your overcharge rate as low as practical in a spacecraft in order to avoid too much heat and temperature effects. Once you get the rate down then the charge efficiency is very low, particularly near the end of charge or overcharge. So, therefore, in order to increase the state of charge in the cell appreciably you have to continue that for a long period of time.

SESSION V

"DOES NICKEL HYDROGEN
REALLY HAVE AN ADVANTAGE
OVER NICKEL-CADMIUM?"

Luther W. Slifer, Jr.
Goddard Space Flight Center

CHAIRMAN'S INTRODUCTORY REMARKS

Luther W. Slifer, Jr.
Goddard Space Flight Center

DEDICATION

The circumstances that bring me to chair this session are most regrettable. I did not know Irv Schulman as well as many of you did; however, in the few meetings we had, I found Irv to be a person who was more than willing to share his technical knowledge and experience, who was forthright in providing his technical judgment and who did not harbor residual personal animosities because of conflicting judgments. I consider these characteristics admirable.

Hopefully, we will apply those principles in this session; freely sharing our technical information, forthrightly expressing our technical judgments, even though they may be in conflict, and finally not considering the conflicts personal.

Therefore, I dedicate this session in memory of Irv Schulman.

INTRODUCTION

Our panel members for this session have all contributed significantly in prior GSFC Battery Workshops and hardly need introduction. They are:

Jim Dunlop, of COMSAT Labs., who is one of the pioneers in nickel-hydrogen cell technology;

Fred Betz, of the Naval Research Laboratory, who flew the first (by an eyelash) nickel-hydrogen battery in space on the Navy Navigation Technology Satellite (NTS-2);

Steve Stadnick, of Hughes Aircraft Co., who was instrumental in development of the Air Force nickel-hydrogen cell; and

Joe Lackner, of the Defense Research Board, Canada, who has extensive experience with nickel-cadmium batteries, including those for the Canadian Communications Technology Satellite (CTS).

Each of these panel members will present a paper as described in the agenda for this session. Following these presentations there will be five additional short presentations on nickel-hydrogen and nickel-cadmium cell technology and then we will convene the panel for a discussion of the session's topic question, "Does Nickel-Hydrogen Really Have an Advantage Over Nickel-Cadmium?"

DISCUSSION

While I have the floor, I would like to elaborate on the session's topic question by asking a set of three related questions.

1. Is Ni-H₂ real or imaginary?

2. Can Ni-H₂ compete with Ni-Cd?

3. Why aren't we flying Ni-H₂?

In the first question, perhaps "apparent" would be a better word choice than "imaginary." The implication of the question is that there is a need to carefully distinguish between actual performance data and projected performance data. In that light, the second question asks whether Ni-H₂ competes with Ni-Cd based on current or projected performance. Finally, if we conclude that Ni-H₂ does compete, why is it not used? The first flight of an Ni-H₂ battery was June 23, 1977 and a second shortly afterward. There have been no subsequent flights of Ni-H₂ cells. Why? It's been more than five years since those first flights.

Related to these questions are subsequent sets of questions to be considered in this session.

I. What is a spaceworthy Ni-H₂ cell?

Does one (or more) exist?

The Air Force cell? The COMSAT cell?

Where is it flyable?

In GEO? In LEO?

Is it ready to fly?

Manufacturable?

Reliable?

With known characteristics?

Amenable to power system design?

II. Where is the Ni-H₂ data base?

How good (useful) is real performance data?

From early generation cells?

From current cell designs?

How reliable is projected performance data?

How good are projections?

How will they be attained?

When?

If we conclude that a spaceworthy Ni-H₂ cell exists, we should be able to define the cell, its performance characteristics and where and how it can be used. To use it a data base is required, not only for the cell itself but also for its interfaces with the power system (for example, how should the battery be charged, discharged, reconditioned, etc.); with the thermal system (how should temperature be controlled? what waste heat must be dissipated?); and with the mechanical system (what are the mounting requirements and restrictions?). If a spaceworthy cell does not now exist, then we have questions as to the projected performance. How, how well, and when will it be attained?

With these many questions in mind, let's now go to the presentations to see which can or cannot be answered.

NI-H₂ BATTERIES FOR COMMUNICATIONS SATELLITES*

J. D. Dunlop
COMSAT Laboratories

INTRODUCTION

For the decade of the 1970's, nickel-cadmium (Ni-Cd) batteries were one of the major lifetime-limiting subsystems for INTELSAT telecommunications satellites, specifically for INTELSAT III and IV. The limitations of these Ni-Cd batteries provided strong economic incentives for battery R&D, which has resulted in the development of Ni-H₂ battery technology.

Ni-H₂ batteries are just now being put into service. All of the remaining INTELSAT V satellites (approximately 10), starting with the next to be launched in early 1983, will use Ni-H₂ batteries. In addition, the next generation of INTELSAT VI satellites, and probably INTELSAT VII and VIII, will use Ni-H₂ batteries. This means that international telecommunications satellites will use Ni-H₂ batteries through the 1990's. It is projected that the lifetime of these batteries will be greater than 10 years at deep depth-of-discharge (DOD), and that the battery subsystem will no longer limit satellite lifetime or communications capability during eclipse periods.

This paper discusses the advantages of the Ni-H₂ battery, as compared with the Ni-Cd battery, for telecommunications satellites.

NICKEL-CADMIUM BATTERIES

To understand the decision to use Ni-H₂ batteries, it is helpful to review the background data on Ni-Cd batteries for the INTELSAT IV, IV-A, and V spacecraft.

NI-Cd CELL DESIGNS FOR INTELSAT IV, IV-A, AND V

Table I summarizes the major differences in the cell designs for the INTELSAT IV, IV-A, and V programs. Two cells from each manufacturing lot of cells used for each program were analyzed, and the average values are presented. The design changes are summarized as follows:

a. Positive electrode. The plaque for the positive electrode is similar for all three designs, with no change. Sinter porosity (89 percent) is high, in part because of corrosion during impregnation. Loading of active material is high (2.35 g of active material per cubic centimeter of void volume for INTELSAT IV) and has not changed significantly. The combination of

*This paper is based upon work performed at COMSAT Laboratories under the sponsorship of the Communications Satellite Corporation.

high sinter porosity and heavy loading of active material causes the positive electrode to expand with cycling, as discussed in greater detail under "Degradation Mechanisms."

b. Negative electrode. The amount of cadmium on a percent-by-weight basis has not changed. Major changes were the use of a silver catalyst with the INTELSAT IV-A cell design and Teflon treatment of the cadmium electrode with the INTELSAT V cell design. Both changes were made to allow the addition of more electrolyte to the partially starved Ni-Cd cell.

c. Electrolyte. Several changes have been made regarding electrolyte. The initial potassium carbonate content of the electrolyte has been reduced, and the quantity of electrolyte has been increased. The concentration of KOH in the electrolyte has been decreased from 33 percent by weight in INTELSAT IV to 29 percent by weight for INTELSAT V.

d. Separator. Nylon separator (Pellen 2505) has been used for all cell designs. The major change was from the Z fold used for INTELSAT IV to the bagging of the positive electrode for INTELSAT IV-A and V.

OPERATIONAL CONSIDERATIONS

Table II compares the Ni-Cd battery operational features for the three satellites. These features include the following:

a. Charging. Constant current charging was used for INTELSAT IV and IV-A, and sequential charging was used for INTELSAT V.

b. Discharging. Constant current discharge was used for INTELSAT IV and IV-A, and constant power discharge was used for INTELSAT V. (Constant power discharge is more severe at end-of-life because of the higher current requirement at end-of-discharge.)

c. Depth-of-discharge. Figure 1 shows the life expectancy for a Ni-Cd battery as a function of the DOD, based on NASA Crain life test data.* These data were obtained with a cell design similar to that for INTELSAT IV. The actual lifetime of the INTELSAT IV batteries on life test at 43-percent DOD was 7-1/2 years, as predicted by the NASA Crain data. End-of-life was defined as the point in time when the battery voltage dropped below an average of 1 V per cell. The lifetime of the INTELSAT IV batteries in orbit was extended beyond 10 years by reducing the DOD to 20 percent or less.

PERFORMANCE

INTELSAT IV Battery

A paper describing the INTELSAT IV Ni-Cd battery orbital performance was presented at the 28th Power Sources Symposium (ref. 1). Battery performance was judged on the basis of the minimum end-of-discharge voltage for the

*Private communications from G. Halpert, NASA Goddard Space Flight Center.

battery, as measured during the eclipse season. A summary of the minimum end-of-discharge voltages for the INTELSAT IV batteries is presented in figure 2. While there is a spread in the data, all of the batteries degrade in voltage performance with time at a similar rate.

The oldest spacecraft in the INTELSAT IV series was the F-2 satellite. Its battery voltage dropped below the 1 V per cell average (25 V) during the 14th eclipse season (fig. 3). TWTs were turned off to keep the satellites operational. Load reductions for the F-2, F-3, and F-4 spacecraft through 1978 are shown in table III.

INTELSAT IV-A Battery

The INTELSAT IV-A batteries are performing highly satisfactorily in orbit to date, as well as on the real-time life test. The major factors contributing to this improved voltage performance for INTELSAT IV-A are as follows:

- a. lower DOD of 39 percent;
- b. reconditioning to a 1.0 V per cell average; and
- c. improved cell design, with more electrolyte in cc/Ah, more over-charge protection, and less carbonate initially in the electrolyte.

Lower DOD, combined with reconditioning to 1.0 V per cell, are felt to be the primary factors in the improved voltage performance observed. The life test battery (now in the 15th eclipse season) is just beginning to show voltage degradation (fig. 4). These batteries are expected to achieve approximately 9 years in orbit at 39-percent DOD.

INTELSAT V Battery

The INTELSAT V battery has completed six eclipse seasons of real-time life test, with good performance to date. It is too early to make any judgment on life expectancy. The 50-percent DOD combined with the constant power discharge is felt to be pushing the state of the art of Ni-Cd battery technology to achieve a 7-year lifetime.

DEGRADATION MECHANISMS

Periodically, cells are removed from the real-time life tests of INTELSAT IV, IV-A, and V for analysis. Of specific interest are changes in the properties, composition, etc., of electrode stack components and electrolyte, which may degrade performance.

Positive Electrode Expansion

Positive electrodes expand with time, as shown in figure 5. The heavy loading of active material (2.36 g/cc void volume), combined with the porous sinter structure, have been reported to cause expansion with cycling (refs. 2 and 3). The data in figure 5 also show that the rate of expansion increases with DOD for real-time eclipse operation. Expansion of the positive electrode results in electrolyte redistribution and eventual shorting of the cells.

Separator Degradation

The rate of carbonate level buildup in the electrolyte has been explained by electrochemical oxidation of nylon solubility products (refs. 4 through 6). Figure 6 shows the K_2CO_3 buildup as a percent of the total electrolyte weight. Note that the INTELSAT IV cell had significantly higher initial carbonate concentration than the INTELSAT IV-A and V cells. The higher rate of increase for carbonate in the INTELSAT IV cell is explained by the higher temperature in storage between eclipse seasons and by the smaller quantity of electrolyte (cc/Ah) initially.

Oxidation of the separator reduces overcharge protection and eventually causes hydrogen gas generation during charging, which results in swelling of the battery pack. Swelling of the cells results in higher internal impedance. In the real-time life testing of INTELSAT IV cells, the cell packs expanded to the extent that the testing was terminated as a safety precaution.

Cadmium Migration

Cadmium migrates from the negative to the positive electrodes at about the same rate for all cells; both those with silver catalysts in the negative electrode and those with Teflon treatment of the negative electrode (fig. 7). The cadmium migrates to the positive electrode as a $Cd(OH)_3$ ion and accumulates on the surface as a $Cd(OH)_2$ crystal. Approximately 4 percent of the cadmium in the negative electrode has migrated to the positive electrode after 14 eclipse seasons. This cadmium migration eventually will cause the cell to short.

ADVANTAGES OF NI-H₂ BATTERIES

Ni-H₂ cells are compared with Ni-Cd cells in terms of their potential advantages for use in communications satellites.

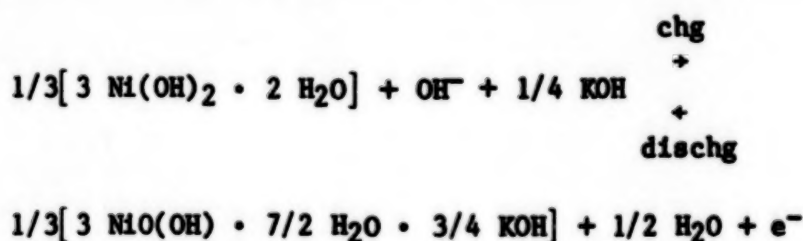
ELECTROCHEMICAL REACTIONS

The electrochemical reactions for both the Ni-H₂ and Ni-Cd cells are presented in tables IV and V, respectively.

Normal Operation

There is no net change in the total amount of water or the KOH concentration while either charging or discharging the Ni-H₂ cell. However, in the Ni-Cd cell, one mole of water per Faraday is produced on charge and consumed on discharge.

It has been recognized by a number of investigators that both the charged and discharged forms of the positive nickel electrodes contain water in what appears to be a loose hydrate. MacArthur (ref. 7), has found a reaction mechanism that involves large changes in the amounts of water and KOH contained in the nickel hydroxide:



For the present INTELSAT V Ni-H₂ cells, the KOH concentration was determined, by analysis, to change from 31 percent in a fully charged cell to between 38 and 42 percent in a fully discharged cell.

The sealed Ni-Cd cell must be designed so that the electrodes are partially starved for electrolyte, to allow for recombination of oxygen at the cadmium electrode (typically 2.0 cc of electrolyte per Ah). With Ni-H₂ cells, gas recombination occurs at the hydrophobic gas interface of the hydrogen electrode. Therefore, the separator and positive electrodes are operated nearly flooded, typically with 3.33 cc of electrolyte per Ah. With the added total amount of electrolyte, the effect of change in KOH concentration is correspondingly reduced.

For the reasons given, it is difficult to make a direct comparison between Ni-Cd and Ni-H₂ cells. However, on any comparable basis, the changes in water content of the electrolyte and in KOH concentration during normal operation will be at least twice as large for the Ni-Cd cell as for the Ni-H₂ cell. This is a significant advantage for the Ni-H₂ cell in terms of cycle life.

Overcharge

Ni-H₂--On overcharge, oxygen is evolved at the positive nickel oxide electrode. This oxygen reacts with hydrogen (which is being produced at equivalent Faradic rates) to form water, and there is no net change in the water content. Thus, this cell has an almost unlimited overcharge capability at charging rates at least four times greater than those of the Ni-Cd system. This is another of the principal advantages of the Ni-H₂ system.

Ni-Cd--On overcharge, the oxygen evolved at the positive electrode must recombine at the cadmium electrode, oxidizing metallic cadmium. This oxidation mechanism is pressure- and temperature-dependent and imposes some difficult design constraints. First, the oxygen must be able to reach the cadmium sites in the negative electrode; thus, this electrode must be partially starved of electrolyte. At the same time, the water content in the electrolyte is greatest at the fully charged condition. This means that the cell is operating in a more electrolyte-starved condition on discharge, which makes the adjustment of electrolyte added to the cell very critical. Secondly, the cadmium electrode must be designed with more capacity than the positive electrode to provide this overcharge protection. For long-life synchronous satellite missions, there are several mechanisms that gradually reduce overcharge protection:

- a. all oxidation mechanisms (such as oxidation of the soluble byproducts of the separator material),
- b. chemisorbed oxygen to the positive electrode,
- c. cadmium migration, and
- d. passivation or decrease in utilization of the cadmium electrode.

Lack of adequate overcharge protection in Ni-Cd cells has been a major contributor to operating difficulties with the INTELSAT III and IV batteries. The INTELSAT IV cells on life test bulged after 7-1/2 years, to the extent that the test had to be stopped. Cell performance deteriorated rapidly as the cells bulged.

Cell Reversal

Ni-H₂--Cell reversal protection is achieved by introducing a hydrogen precharge (i.e., a predetermined quantity of hydrogen gas) into the cell while it is in the discharged state. Under these conditions, the cell becomes positive-limited on discharge. When all the trivalent nickel hydroxide has been reduced in the discharge part of the cycle, continuation of the discharge will cause hydrogen to be evolved at the nickel electrode surface. The evolved hydrogen is compensated for by an equivalent amount of hydrogen that is oxidized at the hydrogen electrode. Thus, the cell can be continuously operated in reversal without a net change in the amount of water in the electrolyte and with no pressure buildup.

Ni-Cd--The cell generates gas in reversal: hydrogen if the cell is positive-limited (as is usually the case); oxygen if it is negative-limited. In either case, a rapid buildup of pressure results due to the small free volume of the cell, and this buildup will eventually result in catastrophic failure.

Summary

For every mode of operation—normal, overcharge, and reversal—there are significant advantages with the Ni-H₂ system.

FAILURE MECHANISMS WITH Ni-Cd CELLS

The failure mechanisms with Ni-Cd cells are as follows:

- a. loss of overcharge protection, pressure buildup, and bulging;
- b. drying out of the separator due to electrolyte redistribution; and
- c. shorting due to cadmium migration.

FAILURE MECHANISMS WITH Ni-H₂ CELLS

The life-limiting failure mechanisms for the Ni-H₂ system in communications satellite applications are still to be determined. Electrode stack components are discussed in terms of stability.

Positive Nickel-Oxide Electrode

The nickel-oxide electrode is the major cycle-life-limiting component in the electrode stack. Nickel-hydroxide electrodes expand with cycling and eventually disintegrate. Expansion is a function of the loading of active material and the DOD.

Electrochemically impregnated positive electrodes are used for the INTELSAT V Ni-H₂ cell design. These electrodes are similar to those used to fabricate the Ni-H₂ cells for the NTS 2 spacecraft. They are electrochemically impregnated by using the Bell Laboratories aqueous process (ref. 8). Laboratory cells using these electrodes have been operated successfully at deep DOD for over 8,000 cycles. Similar laboratory cells that use positive electrodes, such as the INTELSAT IV, IV-A, or V type, fail at about 2,000 cycles. R&D activity is ongoing to fully optimize the nickel-hydroxide electrode for aerospace use.

Asbestos Separator

The asbestos separator material appears to be stable in the Ni-H₂ cell at normal operating temperatures. Analysis of cells from life testing shows no carbonate buildup in the electrolyte, no measurable solubility products, and no change in the physical properties of the separator. Elimination of the potassium carbonate buildup with time is one of the real advantages of the Ni-H₂ cell.

Negative Platinum Electrode

The Teflon-bonded platinum electrode is completely stable. Analysis shows absolutely no change after up to 8,000 accelerated cycles or 7 years on life test.

Electrolyte Redistribution

The Ni-H₂ cell requires a gas volume within the cell. On charge, hydrogen is generated at the negative electrode and passes through the gas diffusion screen into the free volume surrounding the stack. Electrolyte entrainment by the hydrogen gas is a possible loss mechanism. The hydrogen electrode has a hydrophobic Teflon backing, which has stopped electrolyte entrainment loss.

During overcharge, oxygen generated at the positive electrode diffuses out between the back-to-back electrodes. Electrolyte entrainment by the oxygen gas is another possible loss mechanism. Experimental results show no measurable electrolyte entrainment loss during overcharge with the low charge rates used for synchronous satellites. COMSAT has not investigated the back-to-back design for continuous high-rate duty cycles above a C/2 charge rate.

Pressure Vessel Leak

The INTELSAT V Ni-H₂ cell operates at a pressure between 100 and 500 psi. If the cell leaks hydrogen, it will certainly fail.

Crack Propagation--Fatigue cycling of the pressure vessel will eventually cause a leak. Experimental testing at COMSAT Laboratories of one INTELSAT IV cell resulted in failure at 105,750 cycles. This cell had been activated with electrolyte and was cycled between 300 and 600 pounds of hydrogen gas pressure. Failure occurred at the electron beam weld at the negative terminal. This test is being repeated on several additional cells.

Zeigler Seal--To date, no failures have been recorded on either NTS 2 or INTELSAT V cells. Approximately 1,000 cells of this design have been manufactured at Eagle Picher Industries. These cells use a plastic compression seal at both the positive and negative terminals.

Pressure Vessel

The final pressure vessel (fig. 8) has been proof tested at twice the maximum operating pressure. A few cells have failed at one of the weld regions; however, the percentage of cells passing the proof test is greater than 99 percent. No cells have been reported to leak after passing the test.

SUMMARY OF FAILURE MECHANISMS WITH NI-H₂ CELLS

Failure mechanisms with Ni-H₂ cells may be summarized as follows:

- a. expansion of positive electrodes,
- b. electrolyte redistribution, and
- c. pressure vessel leak.

LIFE TEST OF THE NI-H₂ BATTERY

Ni-H₂ cells of the same design as the NTS 2 cells that use electrochemically impregnated positive electrodes have been on life test at COMSAT Laboratories since 1976. These cells have now completed 15 eclipse seasons with a 60-percent DOD on the longest eclipse day. This is 60 percent of the measured capacity at beginning-of-life (fig. 9). For 1 year, between the fifth and seventh eclipse seasons, the battery was discharged daily between each eclipse season, and the voltage deteriorated slightly. From the seventh eclipse season to date, the cells have been operated by simulating typical eclipse operation and voltage performance has been highly satisfactory (fig. 9).

SPECIFIC ENERGY

Specific energy for these Ni-H₂ cells is a function of the cell ampere hour capacity and temperature. Table VI shows cell weights for the INTELSAT V, NTS 2, and 50-Ah cells. All of these cells use the same diameter pressure vessels and mounting hardware. Specific energy and battery weights for the three cell designs are shown in table VII.

SUMMARY OF NI-H₂ BATTERY ADVANTAGES

The advantages of using the Ni-H₂ battery, in comparison to the Ni-Cd battery, are summarized in table VIII.

STATUS OF NI-H₂ BATTERY APPLICATIONS

The first flight batteries for the INTELSAT V F-5 spacecraft are in the final stages of acceptance testing. These batteries are scheduled to be shipped to Cape Kennedy at the end of November 1982 for installation. Launch of this spacecraft is scheduled for early 1983. This will be the first of several spacecraft series (INTELSAT V, V-A, and VI) to use Ni-H₂ batteries for energy storage, and the performance of these batteries in orbit will provide the basis for demonstrating the advantages of Ni-H₂ batteries for use in world telecommunications satellites.

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TABLE I. INTELSAT Ni-Cd CELL DESIGN FEATURES

Features	IV	IV-A	V
Cell capacity			
Measured (Ah)	21	28	38
Theoretical (Ah)	25.9	31.5	45.4
Positive electrode			
Porosity (%)			
Plaque	81	81	81
Sinter	89	89	89
Thickness (cm)	0.078	0.076	0.078
Additives	LiOH	Cd	-
Active material loading (g/cm ³)	2.36	2.35	2.25
Composition (w/o)			
Ni(OH) ₂	51	47	48
Co(OH) ₂	2.2	2.3	2.2
Cd(OH) ₂	-	3.8	2.4
LiOH	0.08	-	-
Negative electrode			
Thickness (cm)	0.089	0.083	0.077
Additives	-	Silver	Teflon
Cd (w/o)	39	39.5	39
Overcharge protection (Ah)	6	11	16
Electrolyte			
KOH (w/o)	24.7	28.5	27.4
K ₂ CO ₃ (w/o)	9.4	4.8	4.4
Volume (cc)	45	61	92
cc/Ah	1.74	1.94	2.03
Original KOH (w/o)	33	31	29
Separator			
Nylon (2505)	Z fold	Bag	Bag
Container			
Wall thickness (mils)	20	20	12
Cell			
Negative/positive	1.6	1.6	1.5
Weight (g)	650	840	1,040
Energy density (Wh/kg)	39	40	44
(avg voltage = 1.2 V)			
Usable energy density (Wh/kg)	16.7	15.6	22.9

TABLE II. INTELSAT Ni-Cd BATTERY OPERATIONAL FEATURES

Features	IV	IV-A	V
Storage			
Mode	Open-circuit charged (changed to trickle)	Trickle	Sequential trickle
Rate	c/44	c/69	c/82 (avg)
Temperature (°C)	20	20	12/6
Reconditioning level	1.15 V/cell	1.0 V/cell	0.9 V first cell
Charging rate	c/18	c/23	c/26 (avg)
Discharge			
DOD (%)	43	39	52
Type	Constant current	Constant current	Constant power

TABLE III. CHRONOLOGICAL EVENTS FOR F-2, F-3, AND F-4 SATELLITES

Event	Time	Load reduction (A)	New load (A)
F-2			
Original	First season (3/71)	—	15.0
Gradual loss	First 7 seasons (3/74)	0.4	14.6
One receiver off	Prior to 8th season (9/74)	0.5	14.1
One TWT off	First tube turned off prior to 12th season (9/76)	1.0	13.1
Two TWTs off	Second tube turned off (3/27/77)	1.0-1.2	11.9
Six TWTs off	Third, 4th, and 5th tubes turned off during 14th season (9/15/77); 6th tube turned off during 14th season (9/23/77)	3.8	8.1
F-3			
Original	First season (3/72)	—	14.5
Gradual loss	First 10 seasons (9/76)	0.5	14.0
Receiver off	Prior to 11th season (3/77)	0.6	13.4
One TWT off	During 12th season (9/15/77)	0.9	12.5
F-4			
Original	First season (3/72)	—	14.3
Gradual loss	First 6 seasons (3/74)	0.3	14.0
Receiver off	Prior to 7th season (3/75)	0.7	13.3
Receiver on	Prior to 8th season (9/75)	0.7	14.0
Receiver off	Prior to 9th season (3/76)	0.8	13.2
One TWT off	Prior to 12th season (9/77)	1.0	12.2

TABLE IV. Ni-H₂ CELL ELECTROCHEMICAL REACTIONS

Normal Operation	
Positive:	$\text{NiO(OH)} + \text{H}_2\text{O} + e \xrightleftharpoons[\text{Chg}]{\text{Dischg}} \text{Ni(OH)}_2 + (\text{OH})^-$
Negative:	$\frac{1}{2} \text{H}_2 + (\text{OH})^- \xrightleftharpoons[\text{Chg}]{\text{Dischg}} \text{H}_2\text{O} + e$
Net reaction:	$\frac{1}{2} \text{H}_2 + \text{NiO(OH)} \xrightleftharpoons[\text{Chg}]{\text{Dischg}} \text{Ni(OH)}_2$
Overcharge	
Positive:	$2(\text{OH})^- \rightarrow 2e + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O}$
Negative:	$2\text{H}_2\text{O} + 2e \rightarrow 2(\text{OH})^- + \text{H}_2$
	$\frac{1}{2} \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$
Reversal	
Positive:	$\text{H}_2\text{O} + e + (\text{OH})^- \rightarrow \frac{1}{2} \text{H}_2$
Negative:	$\frac{1}{2} \text{H}_2 + (\text{OH})^- \rightarrow e + \text{H}_2\text{O}$

TABLE V. Ni-Cd CELL ELECTROCHEMICAL REACTIONS

Normal operation	
Positive:	$\text{NiO(OH)} + \text{H}_2\text{O} + e \xrightleftharpoons[\text{Chg}]{\text{Dischg}} \text{Ni(OH)}_2 + (\text{OH})^-$
Negative:	$\frac{1}{2} \text{Cd} + \text{OH}^- \xrightleftharpoons[\text{Chg}]{\text{Dischg}} \frac{1}{2} \text{Cd(OH)}_2 + e$
Net reaction:	$\frac{1}{2} \text{Cd} + \text{NiO(OH)} + \text{H}_2\text{O} \xrightleftharpoons[\text{Chg}]{\text{Dischg}} \text{Ni(OH)}_2 + \frac{1}{2} \text{Cd(OH)}_2$
Overcharge (normal positive-limited cell)	
Positive:	$(\text{OH})^- \rightarrow \frac{1}{2}(\text{H}_2\text{O}) + \frac{1}{4} \text{O}_2 + e$
Negative:	$e + \frac{1}{2} \text{Cd(OH)}_2 \rightarrow \frac{1}{2} \text{Cd} + (\text{OH})^-$ $\frac{1}{4} \text{O}_2 + \frac{1}{2}(\text{H}_2\text{O}) + \frac{1}{2} \text{Cd} \rightarrow \frac{1}{2} \text{Cd(OH)}_2 \quad (\text{P,T})$
Overcharge (negative-limited cell)	
Positive:	$\text{Ni(OH)}_2 + (\text{OH})^- \rightarrow \text{NiO(OH)} + \text{H}_2\text{O} + e$
Negative:	$\text{H}_2\text{O} + e \rightarrow (\text{OH})^- + \frac{1}{2} \text{H}_2$
Hydrogen gas will be generated at the negative electrode and will build up pressure, because it is not recombined at any significant rate.	
Reversal (positive-limited cell)	
Positive:	$\text{H}_2\text{O} + e + (\text{OH})^- \rightarrow \frac{1}{2} \text{H}_2$
Negative:	$\frac{1}{2} \text{Cd} + (\text{OH})^- \rightarrow \frac{1}{2} \text{Cd(OH)}_2 + e$

TABLE VI. CELL WEIGHTS

Parameter	INTELSAT V (30 Ah)		NTS 2 (35 Ah)		Laboratory test cell (50 Ah)	
	Weight (g)	%	Weight (g)	%	Weight (g)	%
Positive electrode	282.4	31.7	348.6	33.9	480.0	40.0
Negative electrode	32.2	3.6	72.0	7.0	54.7	4.6
Separators	23.0	2.6	35.1	3.4	39.1	3.3
Screens	3.4	0.38	8.0	0.8	5.6	0.5
Electrolyte	134.0	12.4	159.0	15.5	187.0	15.6
End plates	35.1	3.9	34.0	3.3	35.1	2.9
Pressure vessel, internal hard- ware, and seal assembly	379.9	42.7	371.7	36.1	397.3	33.0
Total	890.2	100.0	1,028.4	100.0	1,198.8	100.0

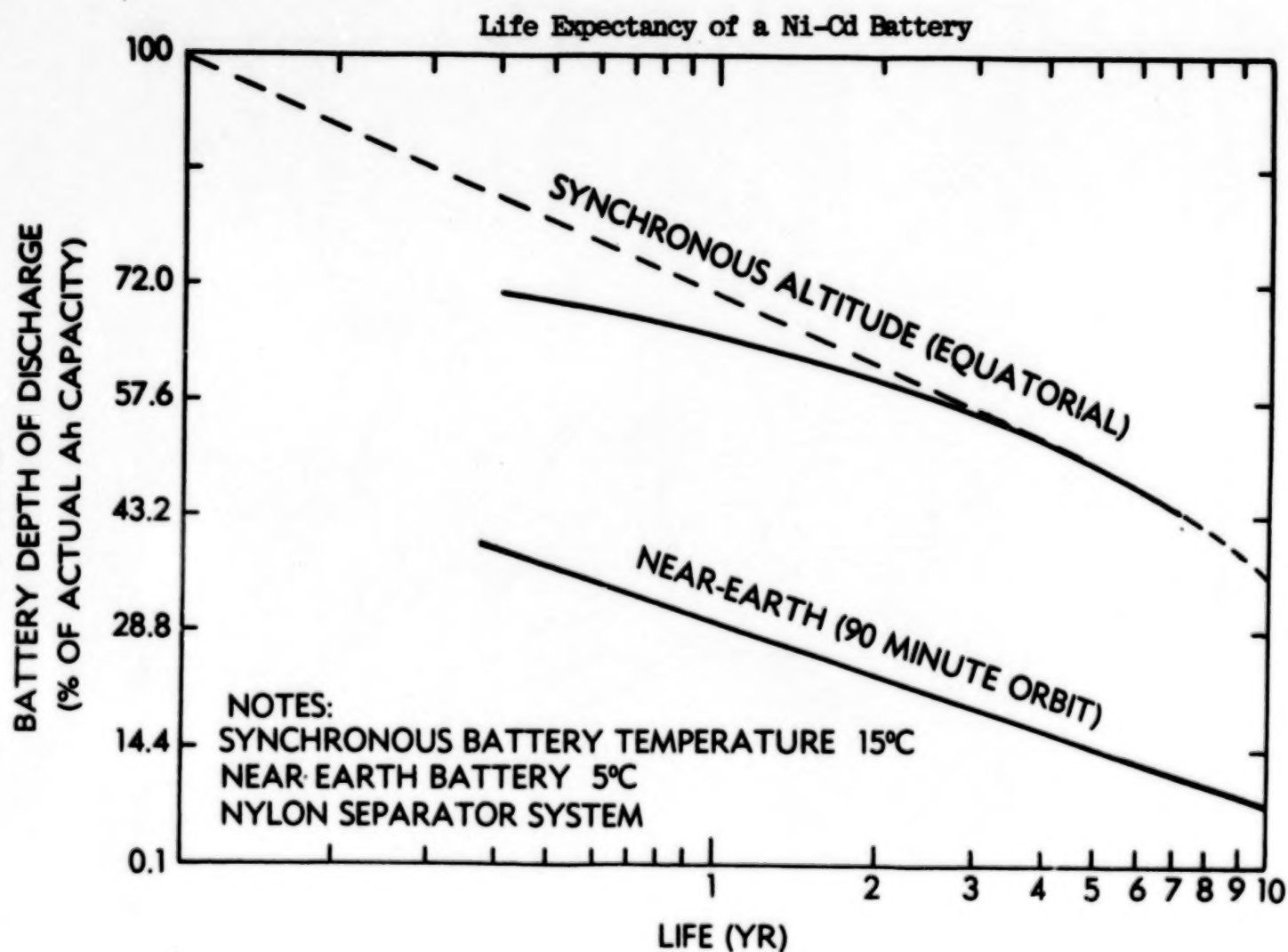
TABLE VII. BATTERY WEIGHT AND SPECIFIC ENERGY

Parameter	INTELSAT V		NTS 2		50-Ah Cell	
	Weight (kg)	%	Weight (kg)	%	Weight (kg)	%
Cell weight	0.890		1.028		1.198	
Cell number	27		14		27	
Total cell weight	24.03	80	14.3	70	32.35	80
Cell mounting shells	3.3	11	3.1	15.2	4.45	11
Base plates	0.73	2.4	1.8	8.8	0.97	2.4
Diode assembly	0.96	3.2	-		1.29	3.2
Mounting hardware	0.10	0.3	0.2	1.0	0.12	0.3
Connectors, etc.	0.23	0.8	1.0	4.9	0.32	0.8
Miscellaneous	0.77	2.6				
Total weight	30.12	100.00	20.50	100.00	40.44	100.00
Energy (Wh at 10°C)	1,174		750		1,944	
Specific energy (Wh/kg)	39.0		36.5		48.1	

TABLE VIII. ADVANTAGES OF THE NI-H₂ BATTERY

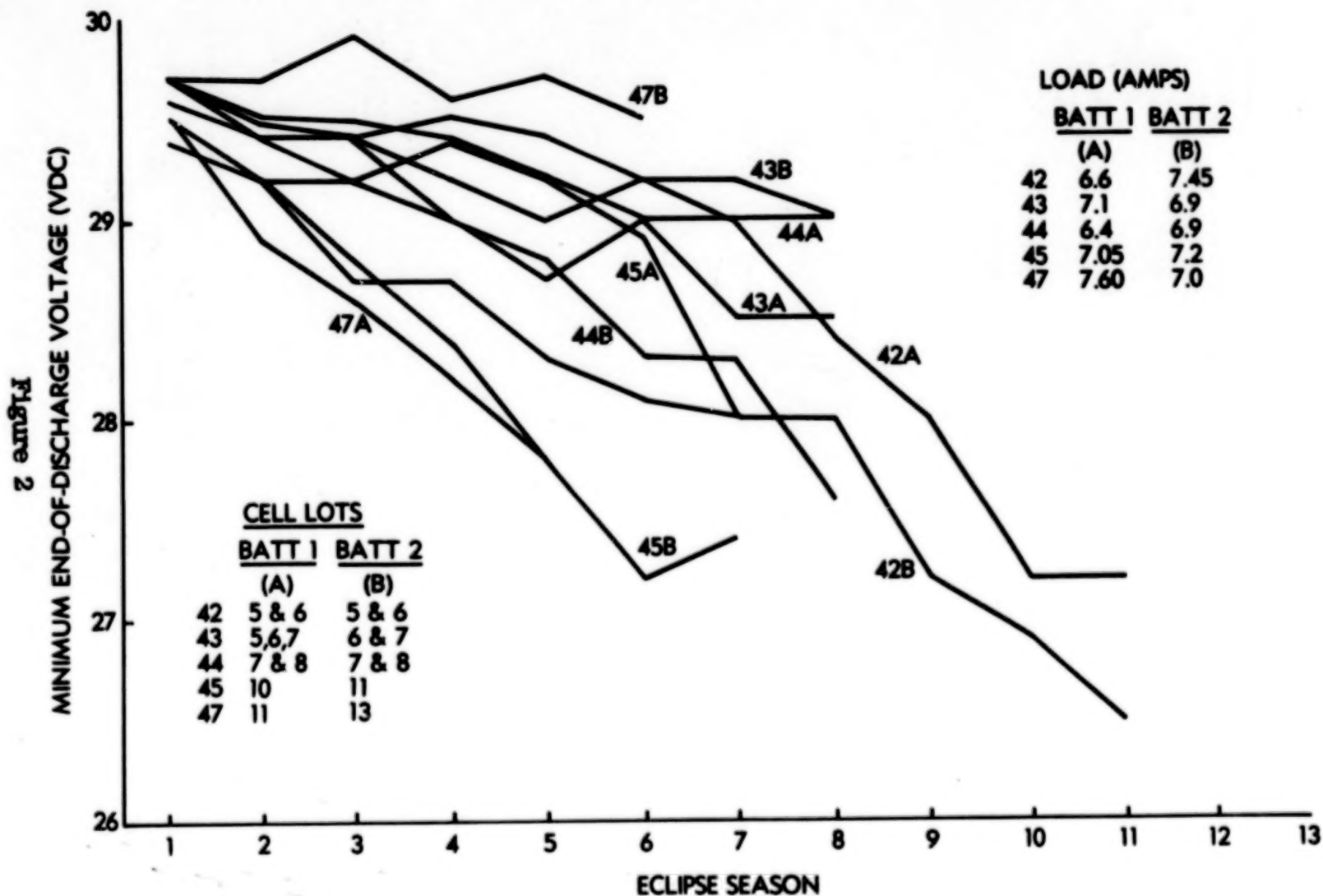
Features	Ni-H ₂	Ni-Cd
KOH concentration change	≈10 percent (significant advantage)	≈15 percent
K ₂ CO ₃ buildup in electrolyte	0 (significant advantage)	1-2 percent/year
Electrolyte	3 cc/Ah (significant advantage)	2 cc/Ah
Redistribution of electrolyte	Entrainment loss	Swelling of electrode
Separator degradation	None	Nylon is soluble in KOH
Negative	No deterioration (significant advantage)	Cadmium migration
Overcharge protection	Unlimited (significant advantage)	Critical, based on excess cadmium
Cycle life at 80-percent DOD	8,000	1,000 + 2,000
DOD for 10-year life	70 percent	45 percent
Usable energy density, 10-year life (for battery)	27-33 Wh/kg	15-20 Wh/kg

Figure 1



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End-of-Discharge Voltage for the INTELSAT IV Batteries



408

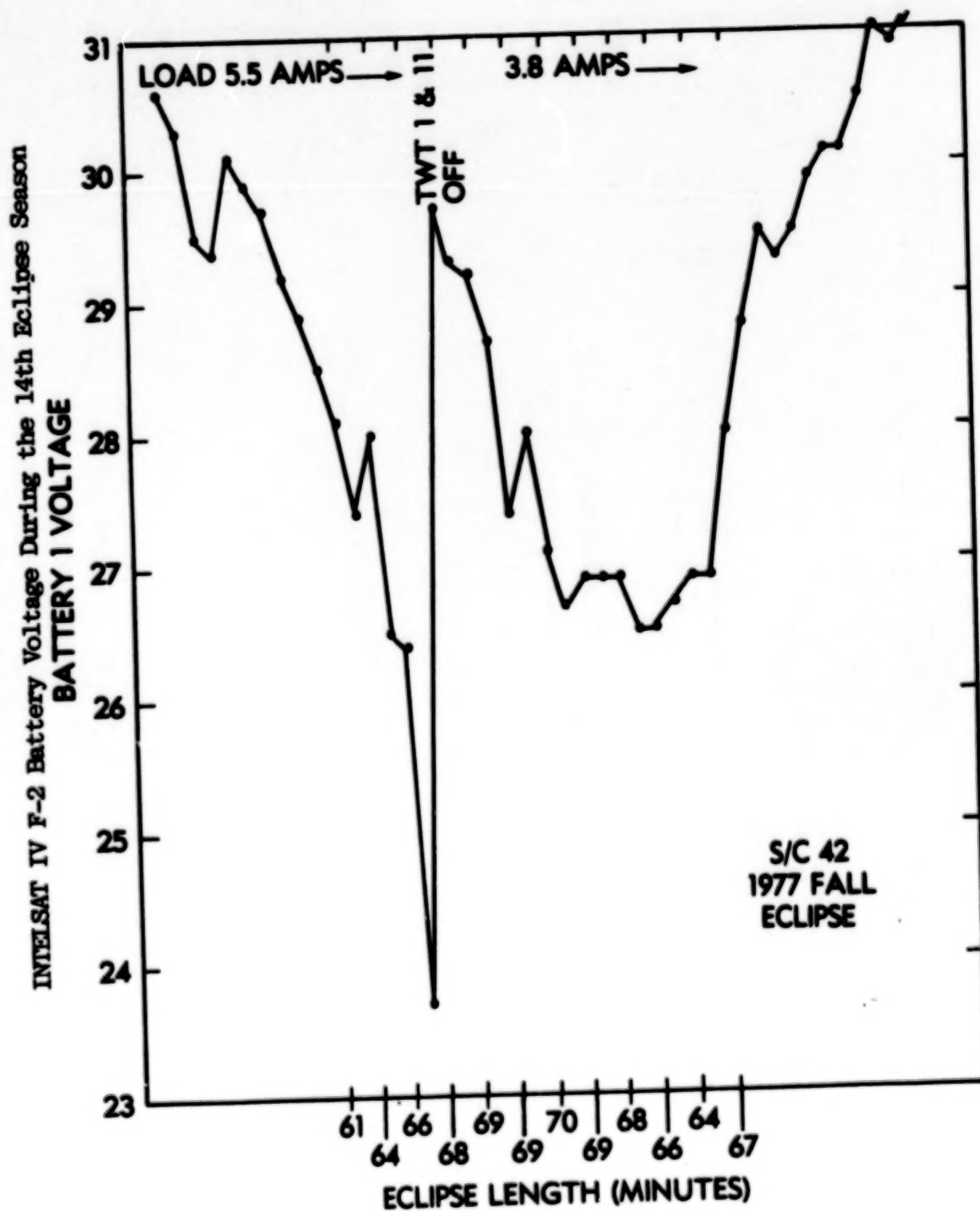


Figure 3

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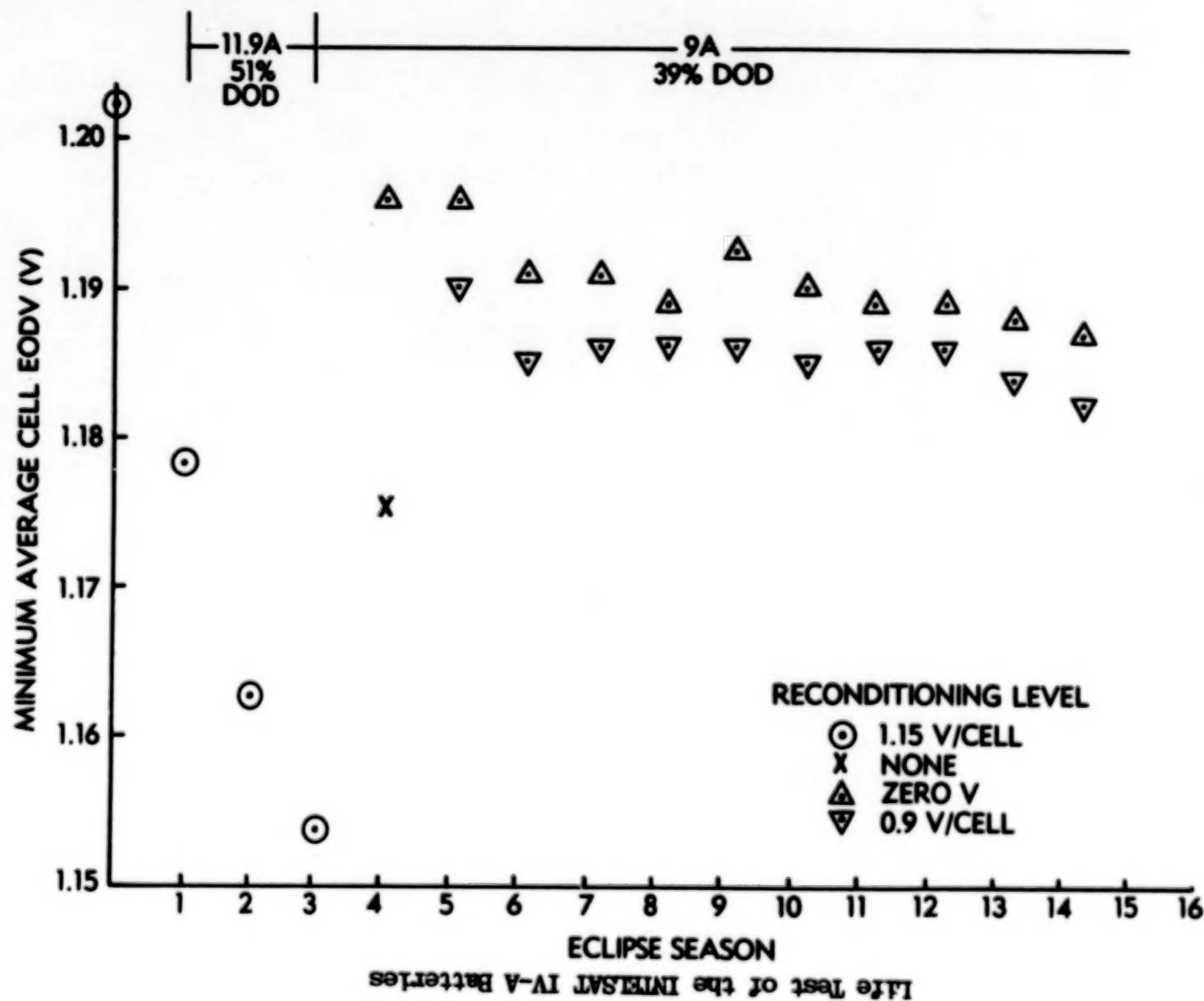
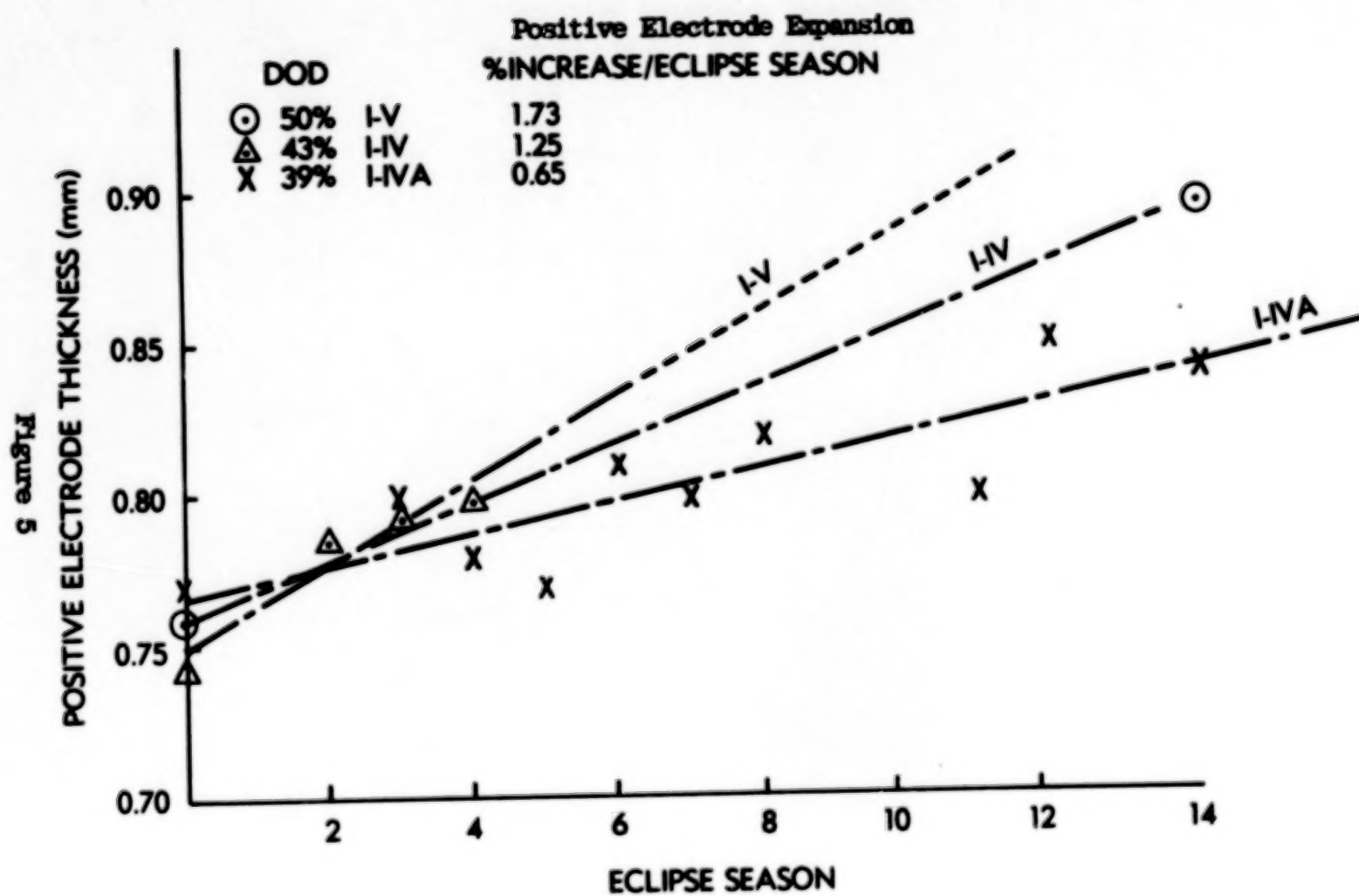


Figure 4



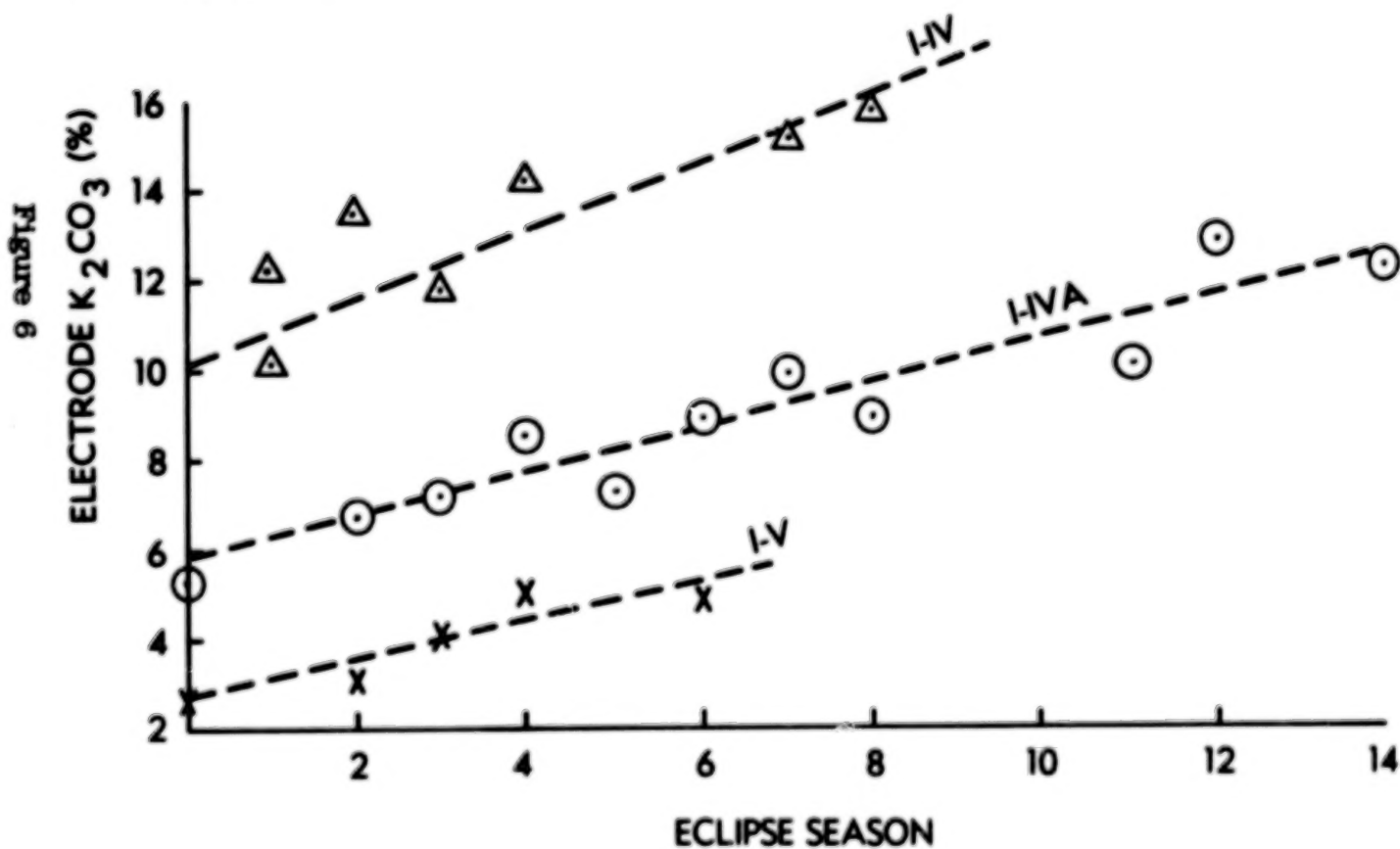
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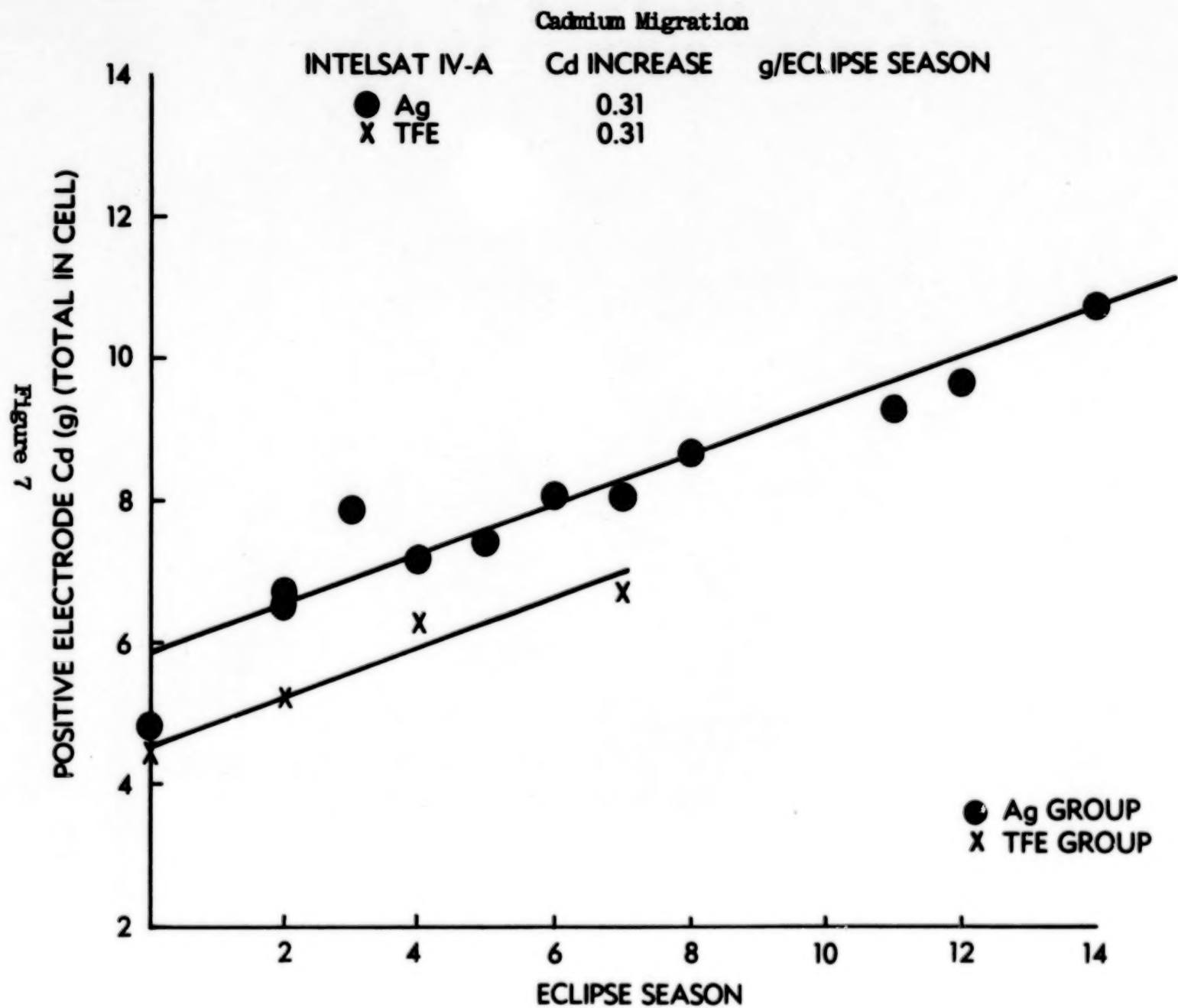
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412

K_2CO_3 Buildup in Electrolyte
INCREASE % K_2CO_3 /ECLIPSE SEASON

0.75 I-V
0.49 I-VA
0.43 I-V





Sketch of Pressure Vessel

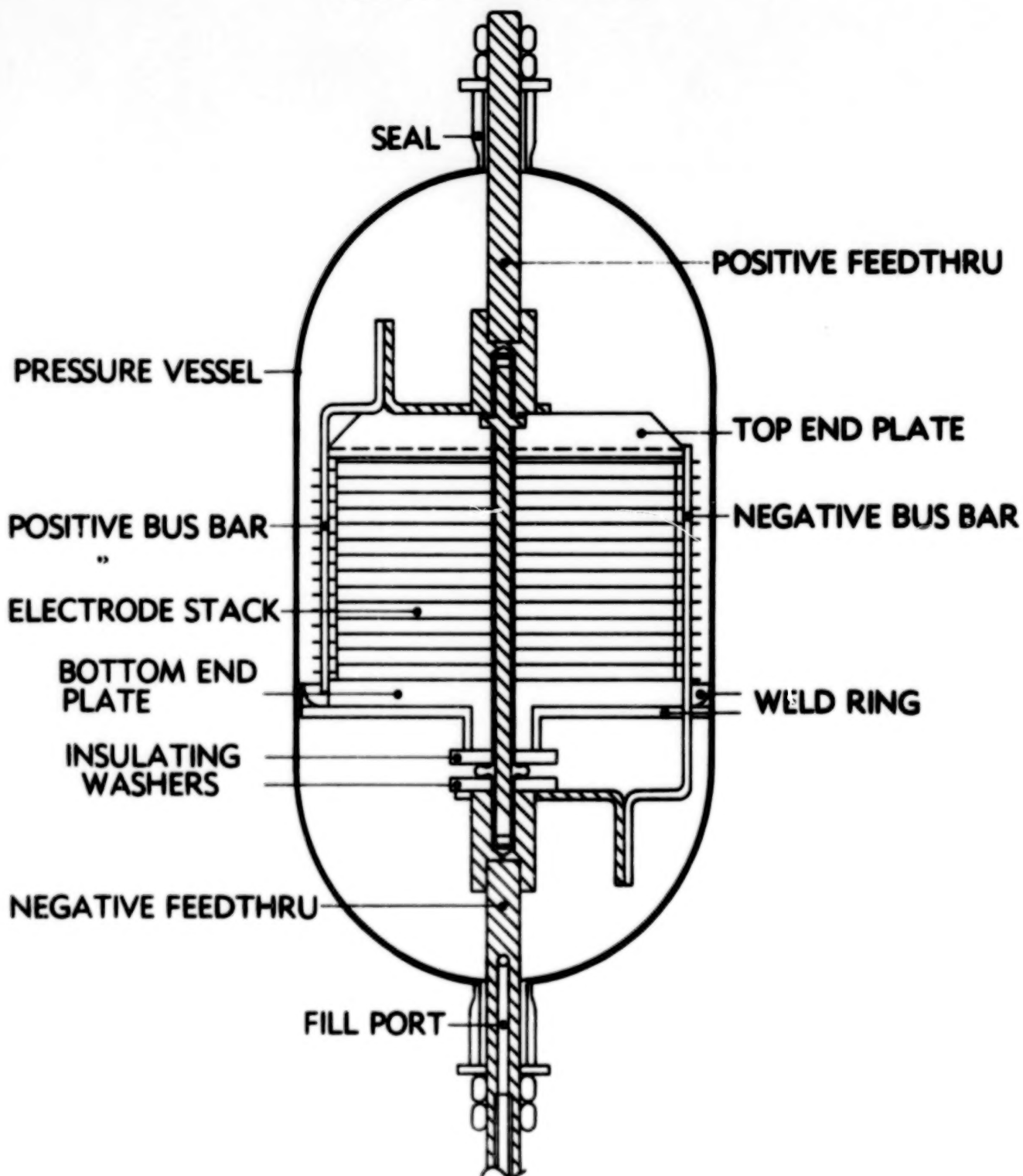
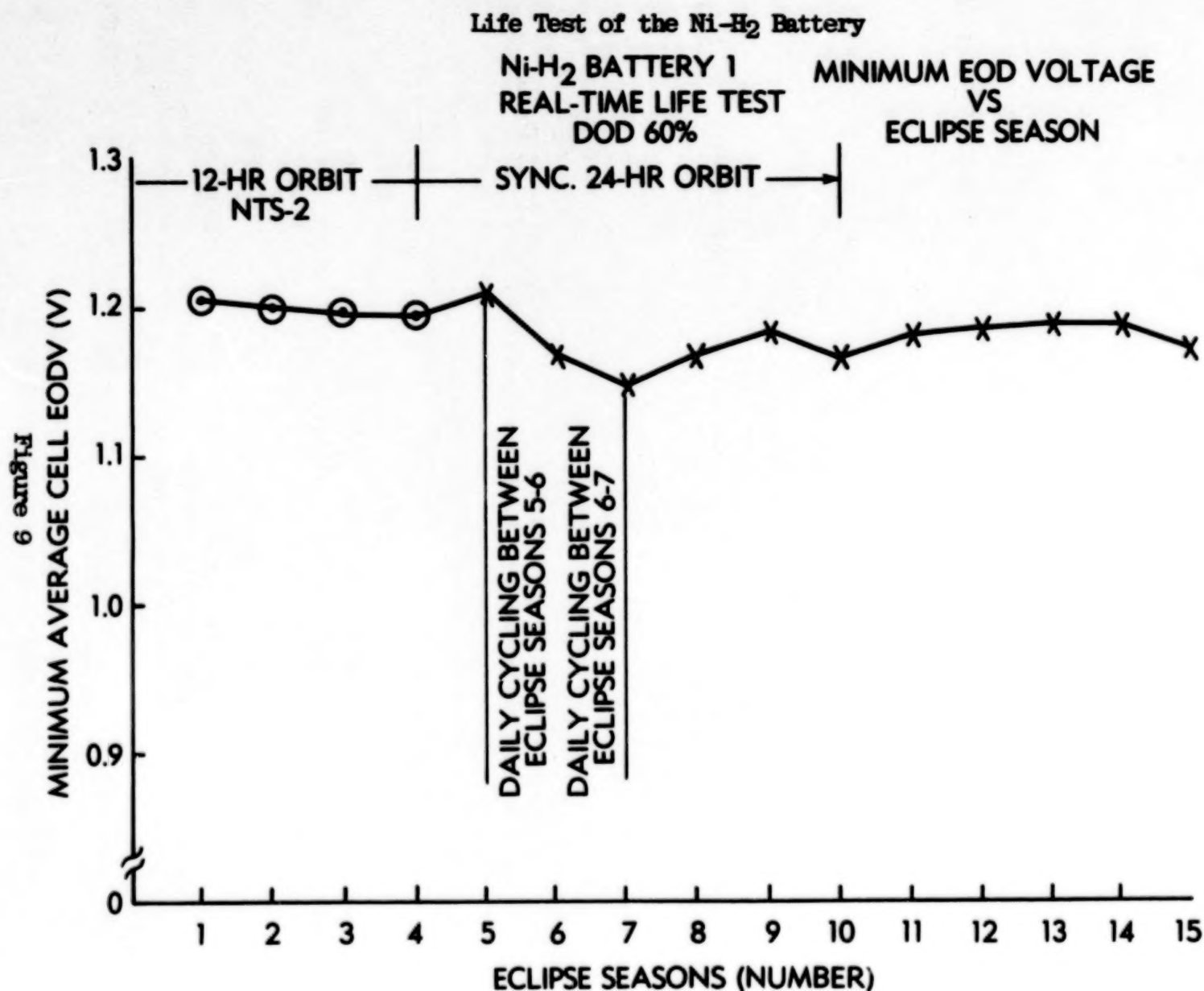


Figure 8



REAL AND POTENTIAL NICKEL HYDROGEN SUPERIORITY

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ABSTRACT

Events from the development and orbital flight experience with a nickel hydrogen battery are described. The events highlight characteristics of nickel hydrogen which afford superior capability in overcharge, overdischarge and state of charge evaluation, when compared to the nickel cadmium electrochemical system. Some developments in nickel hydrogen technology that provide the potential of furthering nickel hydrogen superiority for satellite applications are also discussed.

INTRODUCTION

The Navigation Technology Satellite - Two, (NTS-2), launched in June, 1977 into a 12 hour orbit is now in its twelfth eclipse season. An artist's conception of NTS-2 is shown in Figure 1. The eclipse seasons occur twice a year, with roughly sixty eclipses, reaching a maximum of about 55 minutes, over each 30 day season. The first nickel hydrogen battery in an earth orbiting satellite is aboard NTS-2, and has supported virtually every eclipse load since launch. The battery, consists of two, seven cell assemblies, one of which is shown in Figure 2. Additional background information on the satellite and battery design can be found in references 1 and 2. While some might say that only now is it beginning to equal the capabilities of a nickel cadmium battery, many inherent advantages of the nickel hydrogen system have been observed along the way.

This paper will review specific events in the development and mission life of the NTS-2 nickel hydrogen battery. The events will describe the superior traits of the nickel hydrogen system, or show how a known characteristic can be used for operational advantage. Finally, a few present efforts and developments will be discussed to show the additional potential gain achievable with nickel hydrogen batteries.

REAL SUPERIORITY

OVERCHARGE CAPABILITY

One of the real superior features of the nickel hydrogen cell is its relatively high overcharge capability. For practical purposes the overcharge of nickel hydrogen batteries will be limited by thermal dissipation capabilities of the system, rather than any inherent cell limitations.

With the nickel cadmium battery, a major concern involved the battery overcharge capability. What is the maximum allowable overcharge current as a function of temperature? What maximum oxygen pressure is allowable? What is the maximum allowable voltage for a cell? For a battery? As a function of temperature? These were concerns for good reason. Loss of overcharge capability in a flight nickel cadmium battery could result in battery failure by overpressure and rupture. One can surely recognize the freedom from concern that the nickel hydrogen system affords having conquered overcharge worries.

A tale that should have been forgotten persists about the first installation of the nickel hydrogen prototype into the NTS-2 electrical system. Prior electrical testing had a nickel cadmium battery in the place of the nickel hydrogen. Rewiring of the power harness connector to accept the nickel cadmium battery had been necessary, and was to have been restored to nickel hydrogen configuration before its installation. All but one sixteen gauge wire was correct. Upon mating of connectors, a fully charged, 18 cell, 24 ampere hour nickel cadmium battery was connected in parallel with a fully charged 14 cell, 35 ampere hour nickel hydrogen battery. The condition went undetected for some time until a technician discovered both batteries at the nickel hydrogen battery open circuit potential of about 18 volts. The nickel cadmium battery was fully discharged, had reversed cells and was bulged, the errant wire's white insulation was now brown, and the nickel hydrogen battery was warm to the touch, but otherwise unaffected. The nickel hydrogen battery had accepted the total capacity of the nickel cadmium battery as overcharge, which it simply dissipated as heat.

The excellent overcharge capability was the key to the NTS-2 charger design. The battery radiators were sized to dissipate the heat generated during 0.6 ampere (C/60) trickle charge. Figures 3 and 4 show typical eclipse orbit profiles of voltage, current and temperature. Following an eclipse, the normal charge rate of 3.5 amperes (C/10) would result in battery cooling during efficient charging, and then result in battery heating at the end of charge when heat generation exceeded the radiator capabilities. Normal charge was reduced to trickle charge upon sensing

the rising temperature following full charge. This method of charge control is a heavy handed approach that provides overcharge in excess of that needed for recharge. But it did have the virtue in 1975, of not requiring much other knowledge of the nickel hydrogen system except that it could tolerate the overcharge.

OVERDISCHARGE CAPABILITY

Question: How do you measure the capability of individual cells when they are wired in series in a battery? Answer: Discharge the battery and record the time each cell falls below a specified voltage, terminating the discharge as the last cell falls below the specified voltage. Note: The answer is only applicable to nickel hydrogen batteries. What good fortune for spacecraft battery engineers to have the capability to overdischarge battery cells without any deleterious effect.

While testing the NTS-2 flight battery, a discharge was performed after the battery had been stored charged on open circuit. The purpose was to evaluate variations in "self-discharge" and identify possible "internal shorts". (The test is analogous to the 24 hour open circuitry voltage recovery test for nickel cadmium cells). The discharge proceeded until the capacity of all cells in the battery had been measured and all but two reversed in polarity. The test had been performed with some trepidation, but the results were gratifying and subsequent performance uncompromised.

Having done the reversal on the ground took much of the fright out of observing complete discharge (and assumed reversal) on the NTS-2 nickel hydrogen battery while in orbit; particularly on the second and third complete discharge during the first month in orbit.

The fourth, and most enlightening nickel hydrogen battery overdischarge in orbit occurred at the middle of the seventh eclipse season. Immediately following the eclipse, the satellite inexplicably yawed in the wrong direction, and lost the sun on the solar array. The graph of the nickel hydrogen battery voltage and current is shown in Figure 5 as the event proceeded. Three useful pieces of information can be found from that figure. (1) Battery capacity has not faded with life. Just slightly more than the typical pre-launch 40 ampere hours capacity is found, after allowing for the recharge. (2) Battery voltage, although slightly depressed from the beginning of life condition, does not show the second plateau at 1.10 volt per cell or less typical of the nickel cadmium cell. (3) The steepness of the voltage knee at the end of discharge and lack of cell failure steps in the curve indicates that capacity remains matched, no partially shorted cells are present, and most importantly, the swaged plastic compression seals have not leaked sufficient hydrogen to affect any cell capacity.

STATE OF CHARGE INDICATOR

An additional real superior feature of the nickel hydrogen cell is the state of charge indication obtainable by measuring cell hydrogen pressure. Simple strain gauges, mounted on the cell pressure vessel dome, can be calibrated to provide a signal proportional to the capacity remaining in the cell. How much time and how much money have nickel cadmium investigators spent to find the elusive state of charge of those cells? With nickel hydrogen, it is a fringe benefit. The strain gauges mounted on the NTS-2 nickel hydrogen battery have produced recharge data as shown in Figure 6. Although not put to practical use on NTS-2, state of charge knowledge for satellites with irregular experiment profiles could provide a significant advantage.

POTENTIAL SUPERIORITY

The potential of the nickel hydrogen battery can be glimpsed when you fully recognize that the NTS-2 demonstration was only the first space application. Many things could have gone wrong and in fact many things did go wrong. But the nickel hydrogen battery accommodated the problems, accepted non-optimum operation and is still performing nominally after more than five years in orbit. Only an inherently superior energy storage system could have achieved that record. The ultimate potential of the system is still to be proven.

FAULT TOLERANCE

The reduced concern with overcharge control, the capability to accommodate overdischarge, and the minimal reverse potential during overdischarge are indicative of operational fault tolerance. Inorganic separators and stable, high rate negative electrodes are design factors that improve fault tolerance by reducing wearout modes. The net result is the existence in the nickel hydrogen system of only one failure mode; that of the open circuit cell. Protection for cell open circuits can be accomplished with relays or active electronic devices. Some of the testing of a relay bypass for nickel hydrogen cells was presented at this meeting in 1981 by Dr. Stadnick of Hughes Aircraft Co, (see reference 3). Either way, the system designer is afforded the opportunity to replace redundant battery concepts with redundant cell and bypass techniques. The potential is higher effective utilization and improved energy density of electrochemical storage systems.

CYCLE LIFE

A second area of potential superiority is the yet to be demonstrated cycle life - depth of discharge equation for the nickel hydrogen cell. An extensive data base exists for the nickel cadmium cell cycle life, and virtually none for the nickel hydrogen cell. Many believe that as that data base develops a superior capability for the nickel hydrogen cell will be revealed. The Naval Research Laboratory is currently working to begin a simulated near earth orbital cycling regime to contribute to that data base. The tests will consist of three groups of cells to be cycled at two depths of discharge and two temperatures. Relatively high discharge depths will be used to accelerate the results and establish utilization limits. Six additional cells, obtained at the same time, will be used to evaluate fault tolerant approaches to battery implementation.

COMMON PRESSURE VESSEL CELLS

The concept of the common pressure vessel (CPV) nickel hydrogen battery, as reported by EIC, reference 4, offers a third potential advantage of the nickel hydrogen system. Multiple cells sharing a pressure vessel yield a reduced pressure vessel weight when compared to individual pressure vessel (IPV) cells. CPV batteries will be easier to assemble in higher voltage configuration when the need arises, due to the smaller number of assemblies with which to deal. Finally, the CPV concept can accommodate lower ampere hour capacity configurations without sacrificing energy density to the extent seen with IPV cells. Overall, the CPV promises further improvements in nickel hydrogen energy density.

CONCLUDING REMARKS

The first nickel hydrogen battery in earth orbit is now five and one-half years old and continues to perform satisfactorily. The unique capabilities and advantages of the nickel hydrogen battery offer comfort and relief from many prior concerns of engineers dealing with nickel cadmium batteries. Extensive application of the nickel hydrogen system will require the hard evidence of superior life and energy density advantages over the nickel cadmium system. The accumulation of that evidence is underway today and, I believe, will ultimately result in the acknowledged superiority of the nickel hydrogen satellite battery system.

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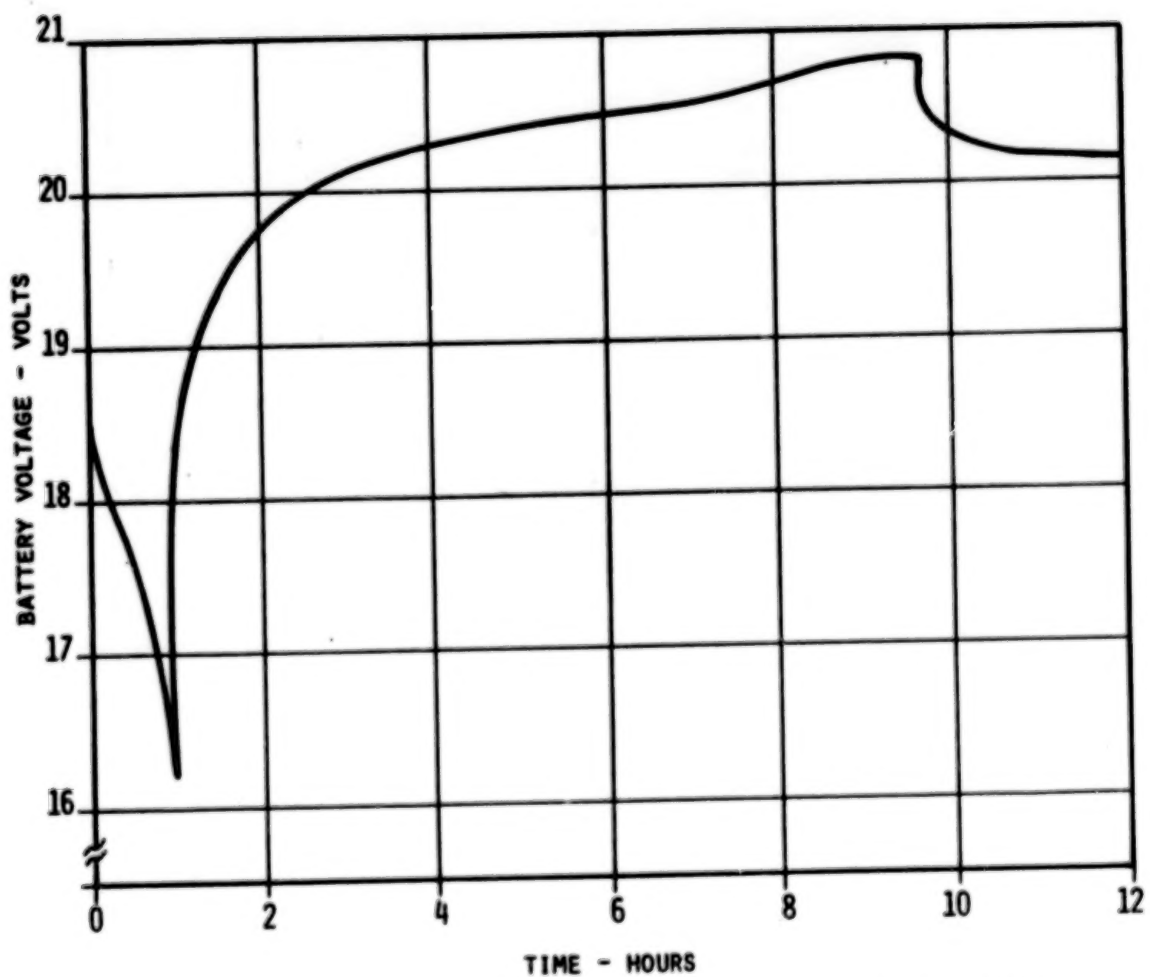


FIG. 3 - BATTERY ORBITAL VOLTAGE CHARACTERISTIC, MIDDLE OF ECLIPSE SEASON 2

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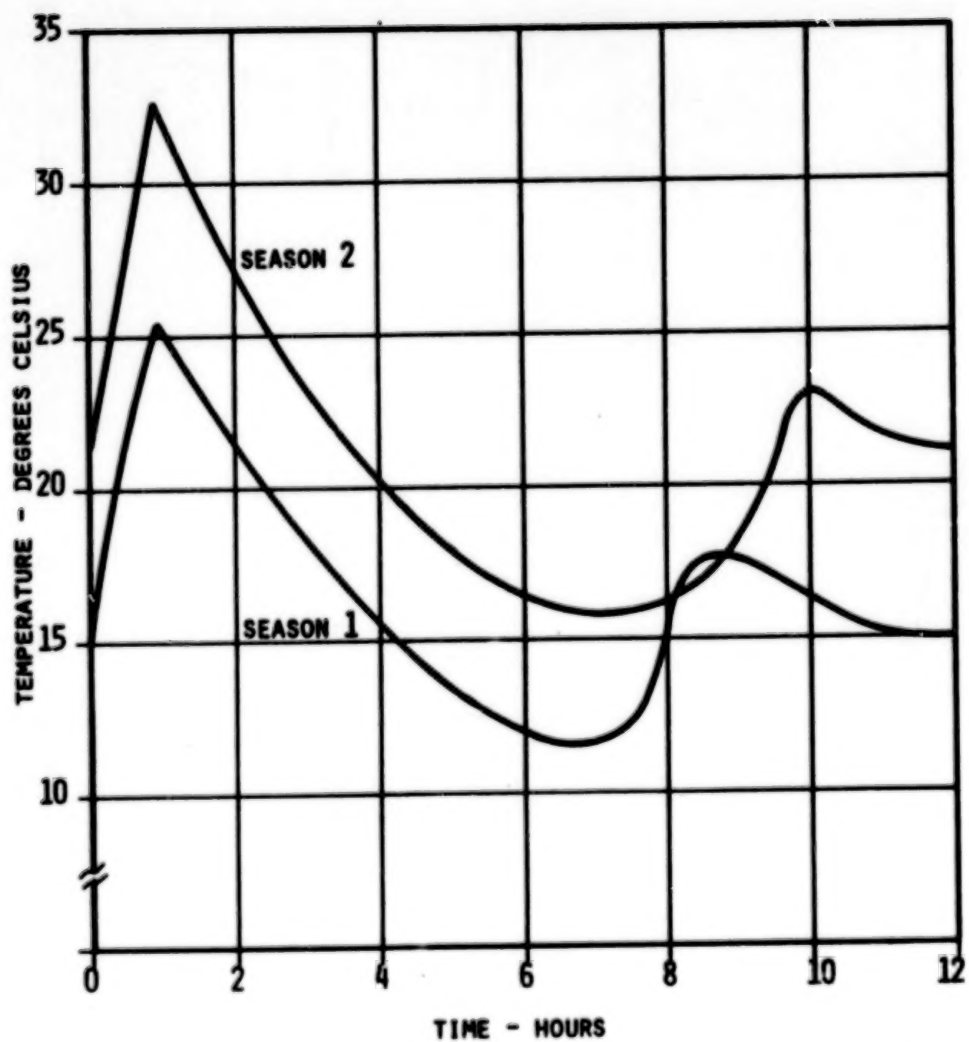


FIG. 4 - NICKEL HYDROGEN BATTERY MID-ECLIPSE SEASON ORBITAL TEMPERATURE PROFILES

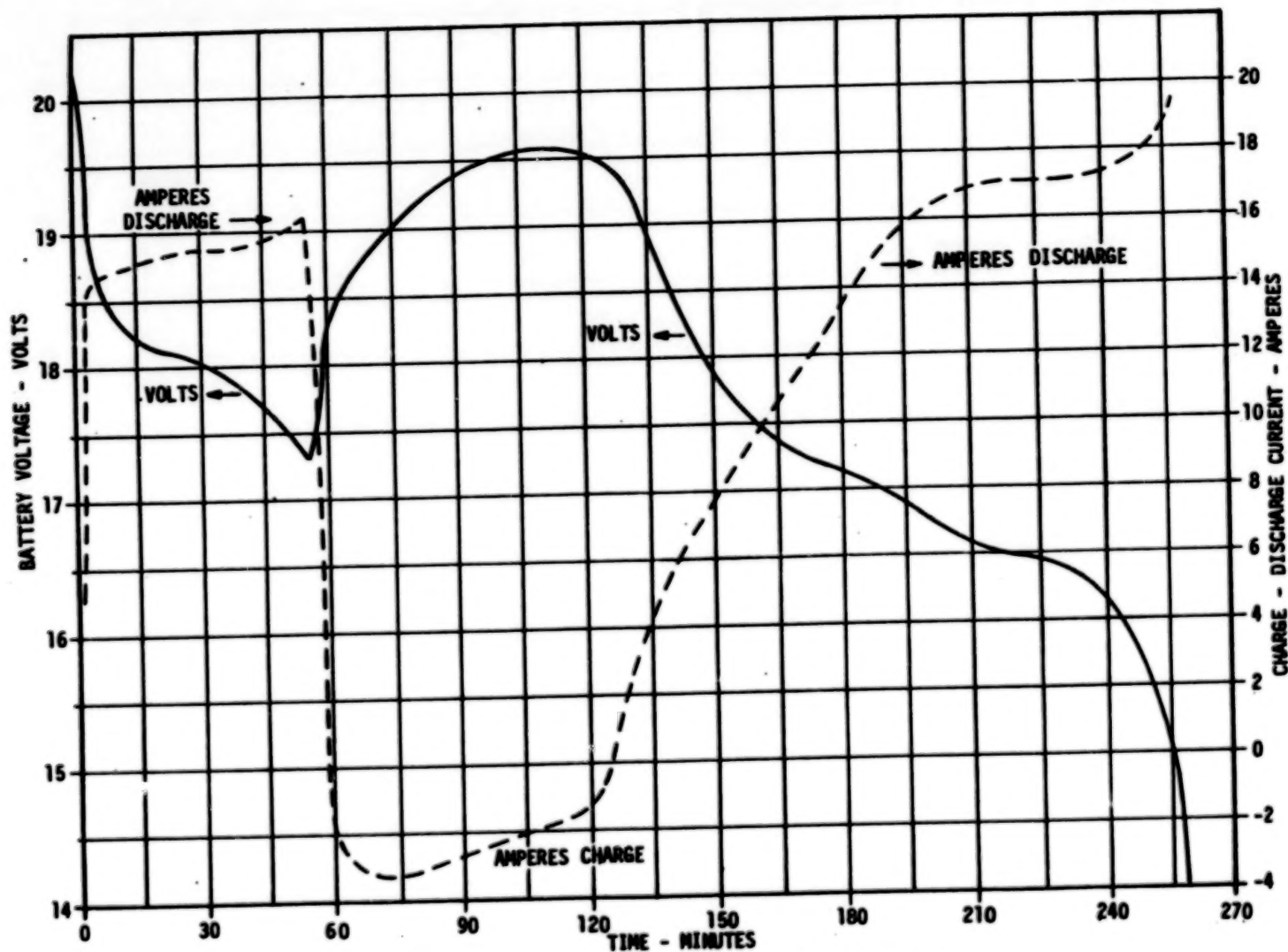


FIG. 5 - NTS-2 NiH₂ BATTERY COMPLETE DISCHARGE SEASON 7 REV 2207

496

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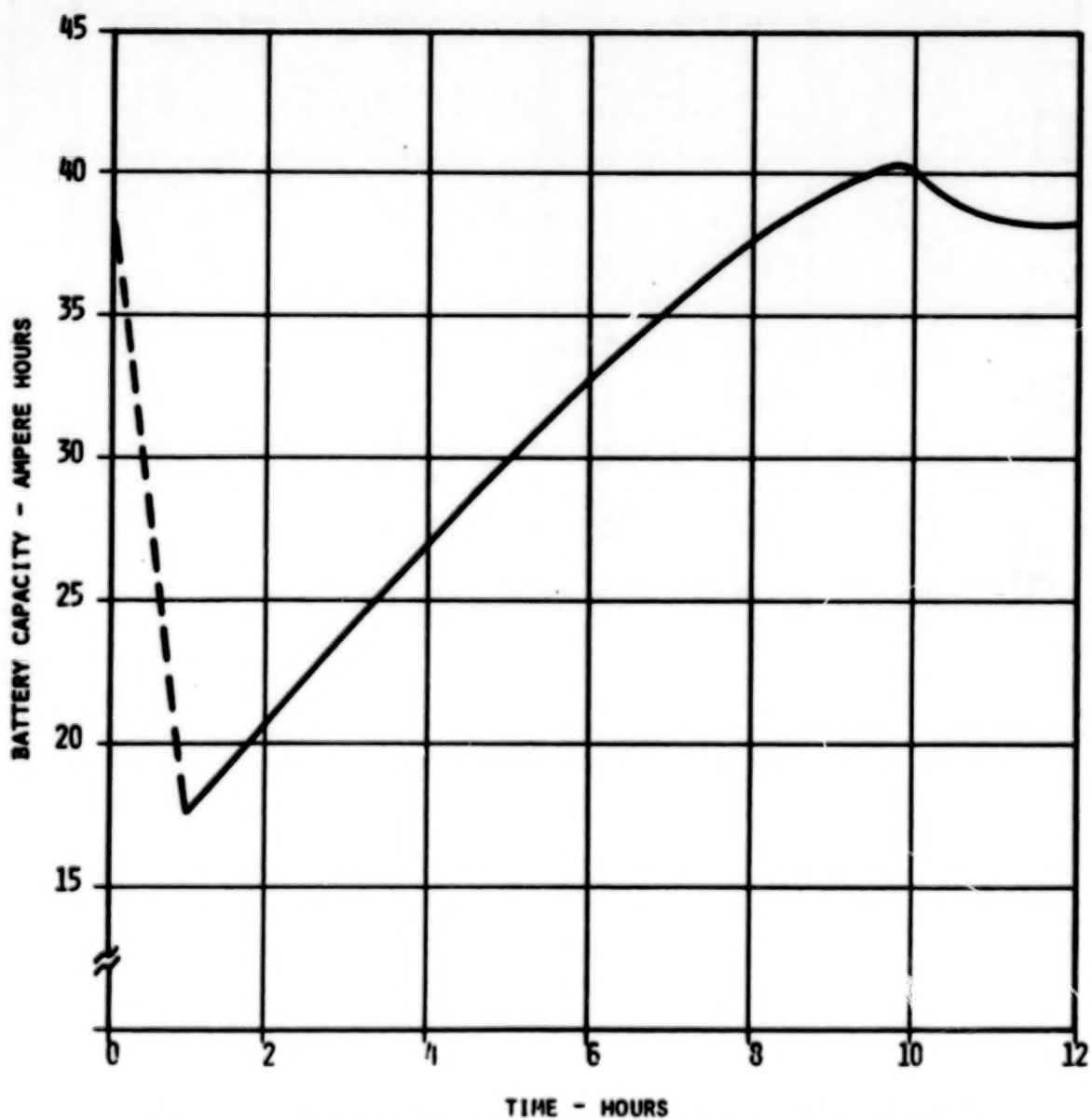
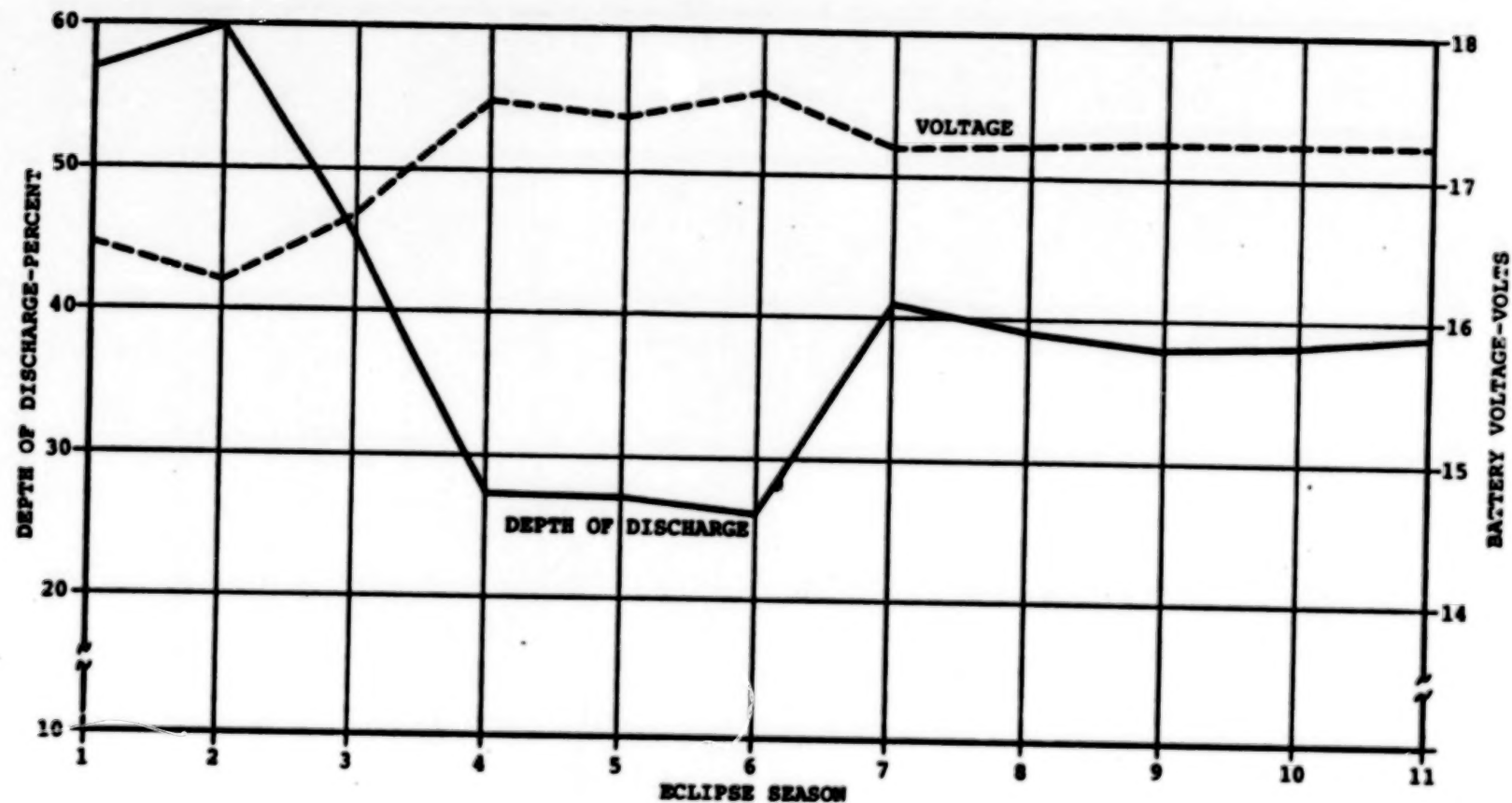


FIG. 6 - ORBITAL BATTERY CAPACITY DERIVED FROM CELL STRAIN GAUGE OUTPUT

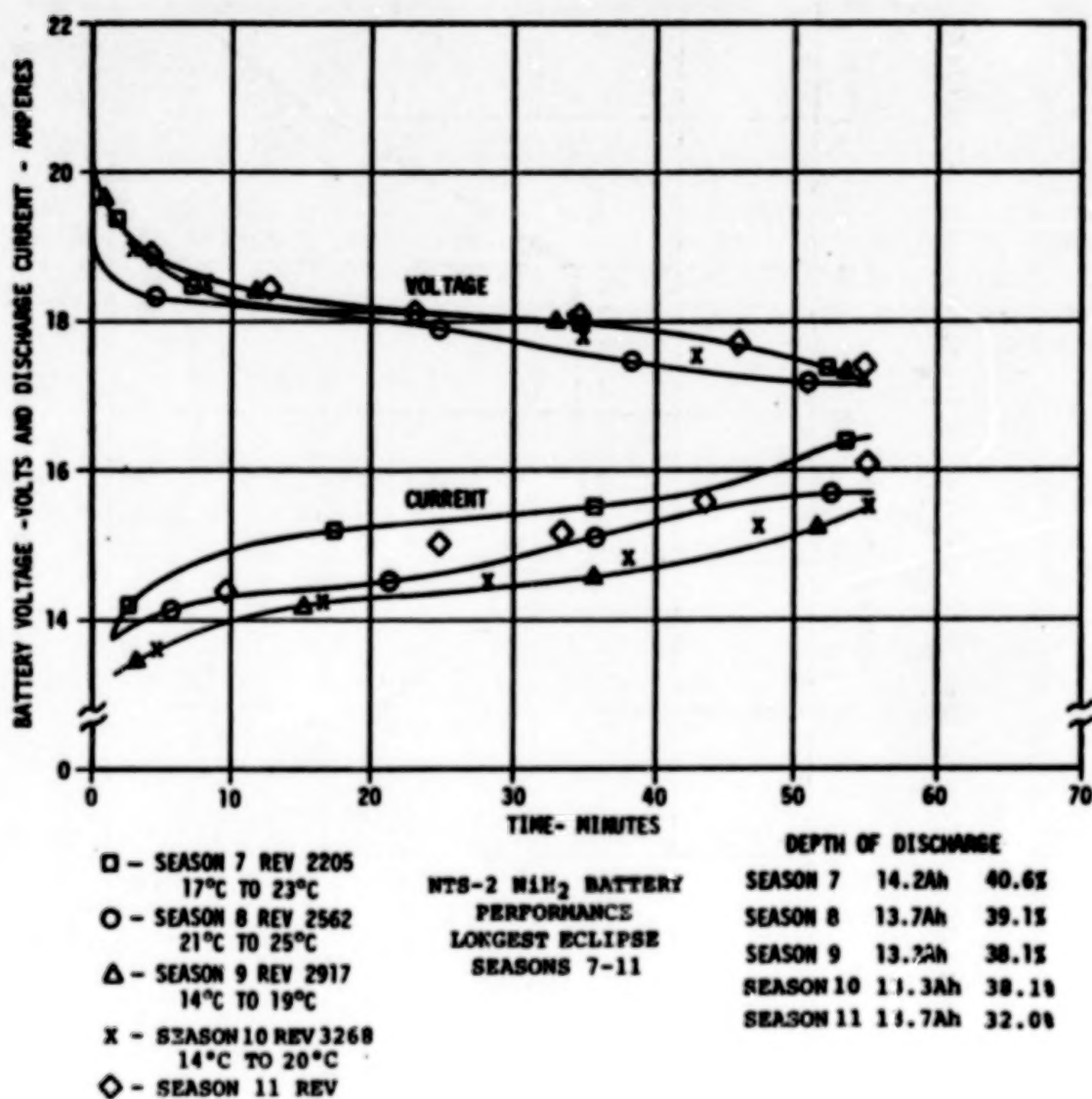


WTS-2 NICKEL HYDROGEN BATTERY
MAXIMUM DEPTH OF DISCHARGE AND MINIMUM DISCHARGE VOLTAGE VS. ECLIPSE SEASON

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428

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NICKEL HYDROGEN/NICKEL CADMIUM BATTERY TRADE STUDIES

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ABSTRACT

Nickel Hydrogen cell and battery technology has matured to the point where a real choice exists between Nickel Hydrogen and Nickel Cadmium batteries for each new spacecraft application. During the past few years, a number of spacecraft programs have been evaluated at Hughes with respect to this choice, with the results being split about fifty-fifty. The following paragraphs contain criteria which were used in making the battery selections.

DESIGN

The design of the Nickel Cadmium and Nickel Hydrogen systems traded are shown in Figures 1-3. Figure 1 is a typical NiCd battery pack for synchronous orbit use. Figure 2 shows the general construction of a NiH₂ cell of the Hughes/Airforce design, and Figure 3 shows a typical cell mounting arrangement where cells are mounted into thermal collar and flange arrangement, which are then inserted into cutout hole in a battery mounting honeycomb panel. The thermal coupling is by radiation in both the NiCd and NiH₂ designs.

WEIGHT

The main driver toward the battery type selection was the weight of the proposed systems. The anticipated decline in the importance of weight as a spacecraft design driving parameter with the use of the space shuttle has never materialized. The weight of the battery remains the most important criteria for choosing a battery system.

As a generality, for spacecraft in synchronous or 12 hour orbit, the range below 1,000 watts of eclipse power is where nickel cadmium batteries are more weight efficient. In the region between 1000 and 1500 watts, the weights are approximately equal, and above 1500 watts, the nickel hydrogen batteries are clearly more weight efficient. This relationship is shown for as typical series of spacecraft applications in Figure 4.

The specific weight of the system depends on the type of nickel hydrogen battery configuration chosen for evaluation. In general, because pressure vessel and packaging weight are related more to the number of cells rather than the capacity, for a given power boost system using 16 to 18 cells is always more weight efficient than a buck system with 31 or 32

cells per battery.

COST

The second most important variable is cost of the total battery power subsystem. In recent years, the relative high cell costs of nickel hydrogen due to limited production has discouraged its use. However, recent increases in the number of cells has produced a reduction in the per cell cost by approximately a factor of two in the Hughes produced nickel hydrogen cell. At this price level, the cost of a NiH_2 battery system is competitive with a NiCd at power levels above approximately 1000 to 1500 watts. Relative cost projections based on current costs for NiH_2 and NiCd systems are shown in Figure 5.

Again, the cost of a NiH_2 system is strongly dependent on the number of cells used, and systems that favor smaller numbers of larger capacity cells are less expensive. Programs now underway, such as the Air Force sponsored Manufacturing Technology program at Yardney hold the possibility of further reductions in the cost of individual cells. Some costs, such as those related to the increased tolerance of NiH_2 cells to overcharge, reversal, calendar life, and temperature, are difficult to estimate. However, in each case of evaluating possible costs in terms of parameters such as overcharge tolerance, the NiH_2 is less expensive due to its greater tolerance and likelihood to survive given circumstances. In general, experience has shown that NiH_2 is more tolerant of electrolyte fill, temperature of operation as related to battery life, depth of discharge, overcharge, and reversal. It also has a "built in" state of charge indicator in the hydrogen gas pressure. The only areas where NiCd cells are more effective is at low charge rates (c/10 and lower) and higher temperatures, (greater than 20°C) where the charge efficiency of the NiCd is higher than a NiH_2 battery.

LIFE

Calendar life is another prime consideration in the selection of a battery system. In general, NiCd batteries are capable of withstanding 10 years of in orbit cycling provided they are well treated. For lives in excess of 10 years, or in circumstances where the batteries will experience unusual demands, NiH_2 are more durable due to the relative few degradation mechanisms present in the cell. The positive electrode appears to be the life limiting component of a NiH_2 cell, and improvements in positive electrodes and the available data base are expected to show that NiH_2 batteries will perform well in excess of 10 years.

VOLUME

The volume occupied by the battery is an important consideration for smaller spacecraft. Low power spacecraft of the Anik-SBS type are typically very volume limited and a NiH_2 battery is almost impossible to install. Shuttle optimized spacecraft currently have sufficient volume that the inclusion of the high volume NiH_2 battery does not present a design problem. However, for higher power spacecraft in the 25KW range, preliminary studies show volume and heat rejection are again important parameters. Figure 6 shows a volume comparison of NiH_2 and NiCd battery volume.

Growth Capabilities

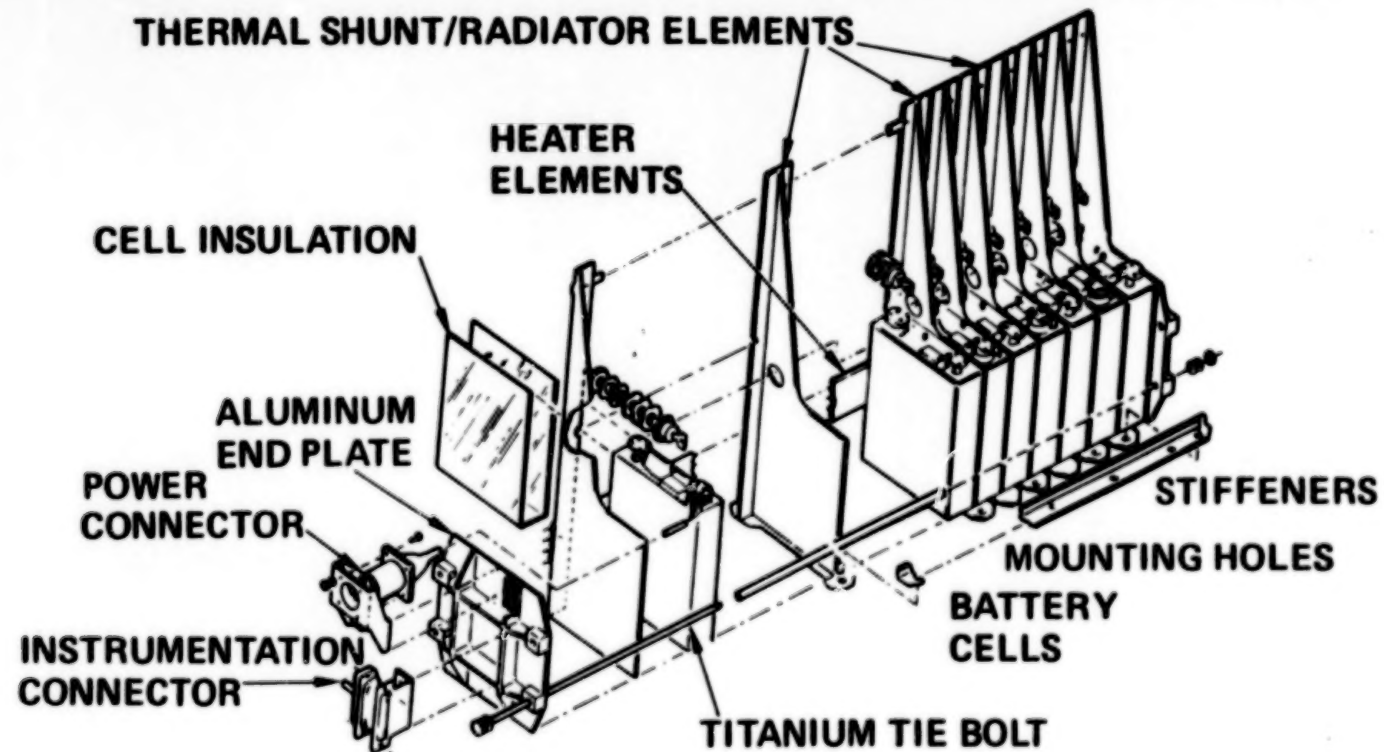
In general, NiCd cells are available in a limited range of capacities, while NiH₂ shows the potential for a wide range of abilities within a specific pressure vessel diameter. As a result is usually easier to increase NiCd power by adding additional cells and to increase NiH₂ power by adding more capacity to each cell. The useful range of 3.5 inch diameter NiH₂ cell is between 15 and 50 AH. The projected useful range for 4.5 inch diameter NiH₂ cells is 50 and 150 AH. Changing the cell capacity within a specific diameter cell is a relatively easy matter.

DATA BASE

Data base for any specific cell design, whether NiH₂ or NiCd, is always a difficult question. Life projections are invariably based on a combination of accelerated test data, real time test data from cells, and analysis of the cell's failure mechanisms. In the case of NiH₂ cells, the long term cell performance is based on a few real tests with test series presently exceeding nine years of real time. Consequently, life projections for NiH₂ cells are based on much analysis and projection than are life projections for NiCd cells. Fortunately, the NiH₂ cells have relatively few wear out mechanisms. The life of the cell is principally determined by the life of the electrode.

In conclusion, the three major selection criteria of weight, power, and life favor NiCd batteries for synchronous spacecraft of less than 1500 watts and 10 years and NiH₂ batteries for spacecraft greater than 1500 watts.

NICKEL-CADMIUM BATTERY PACK DESIGN



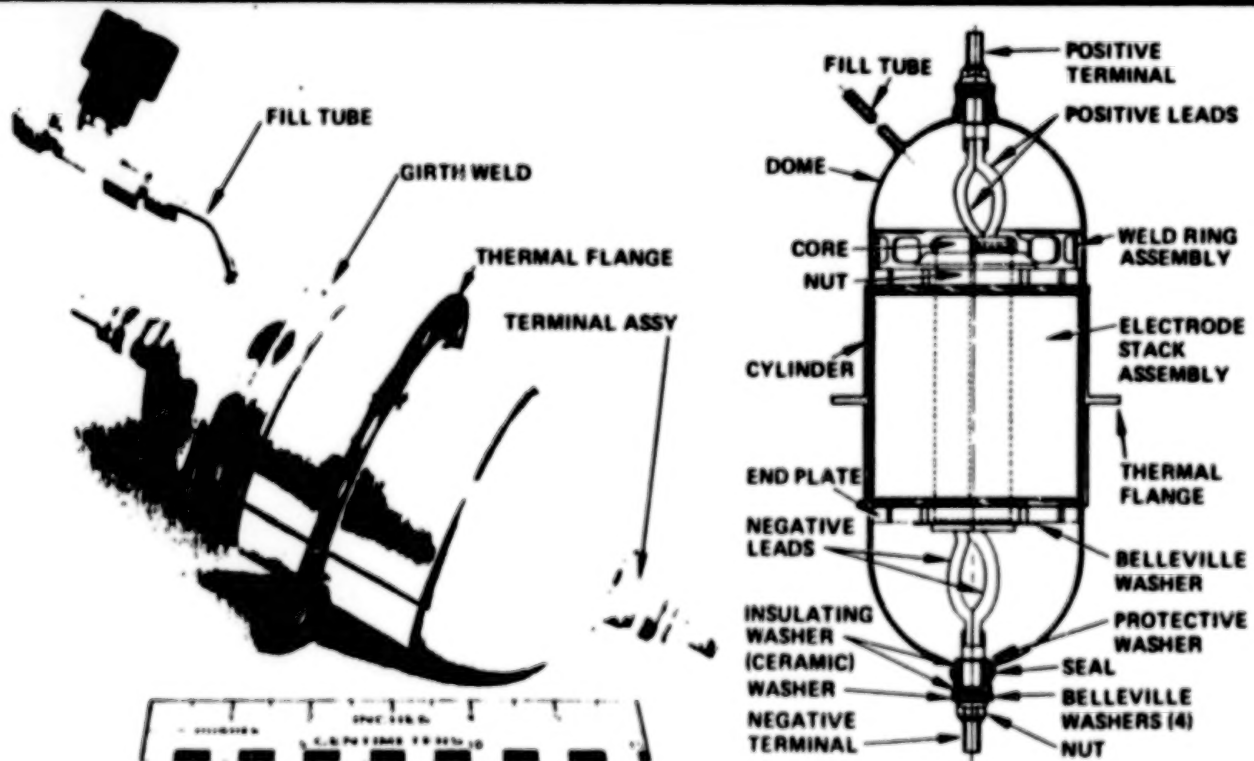
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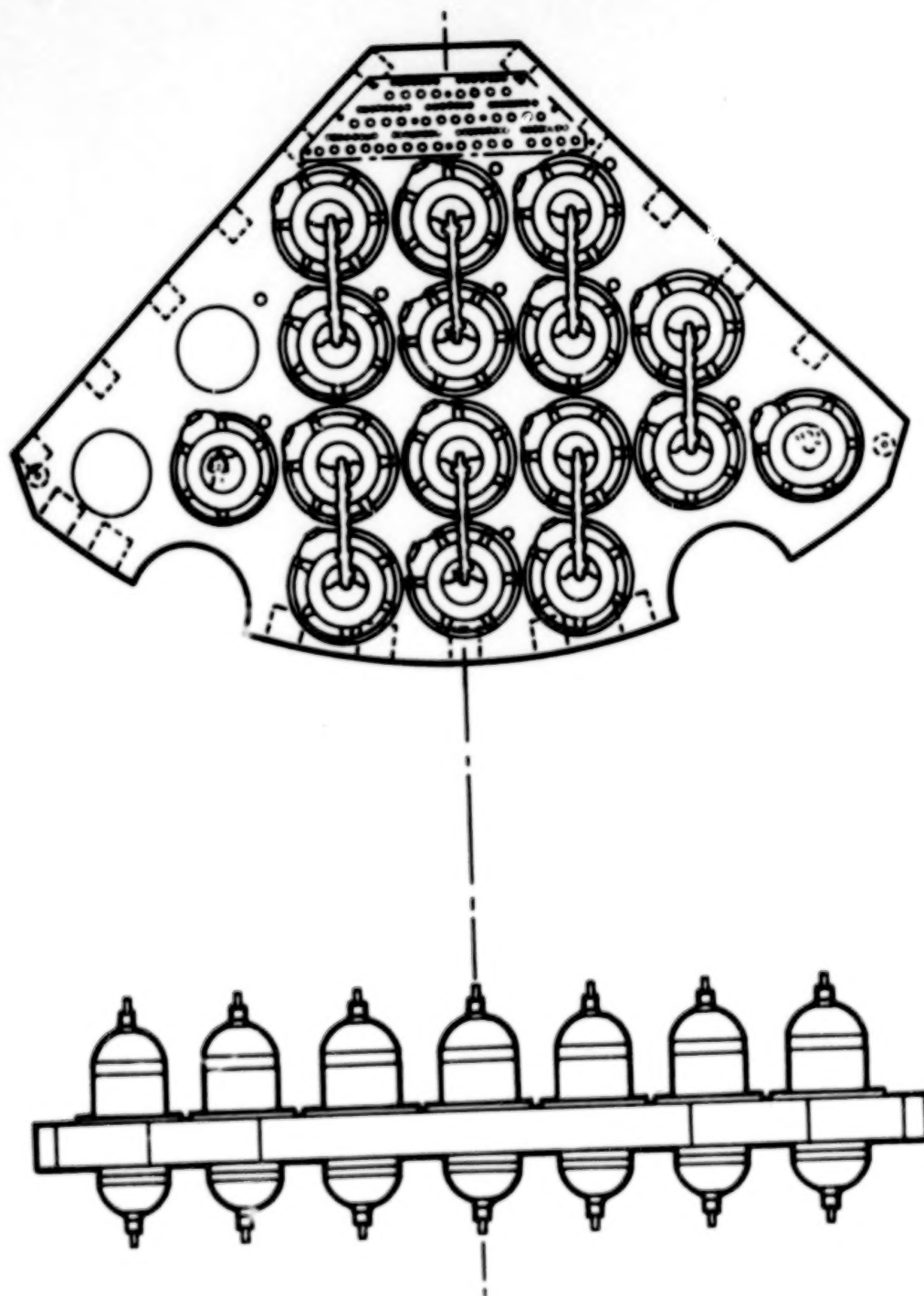
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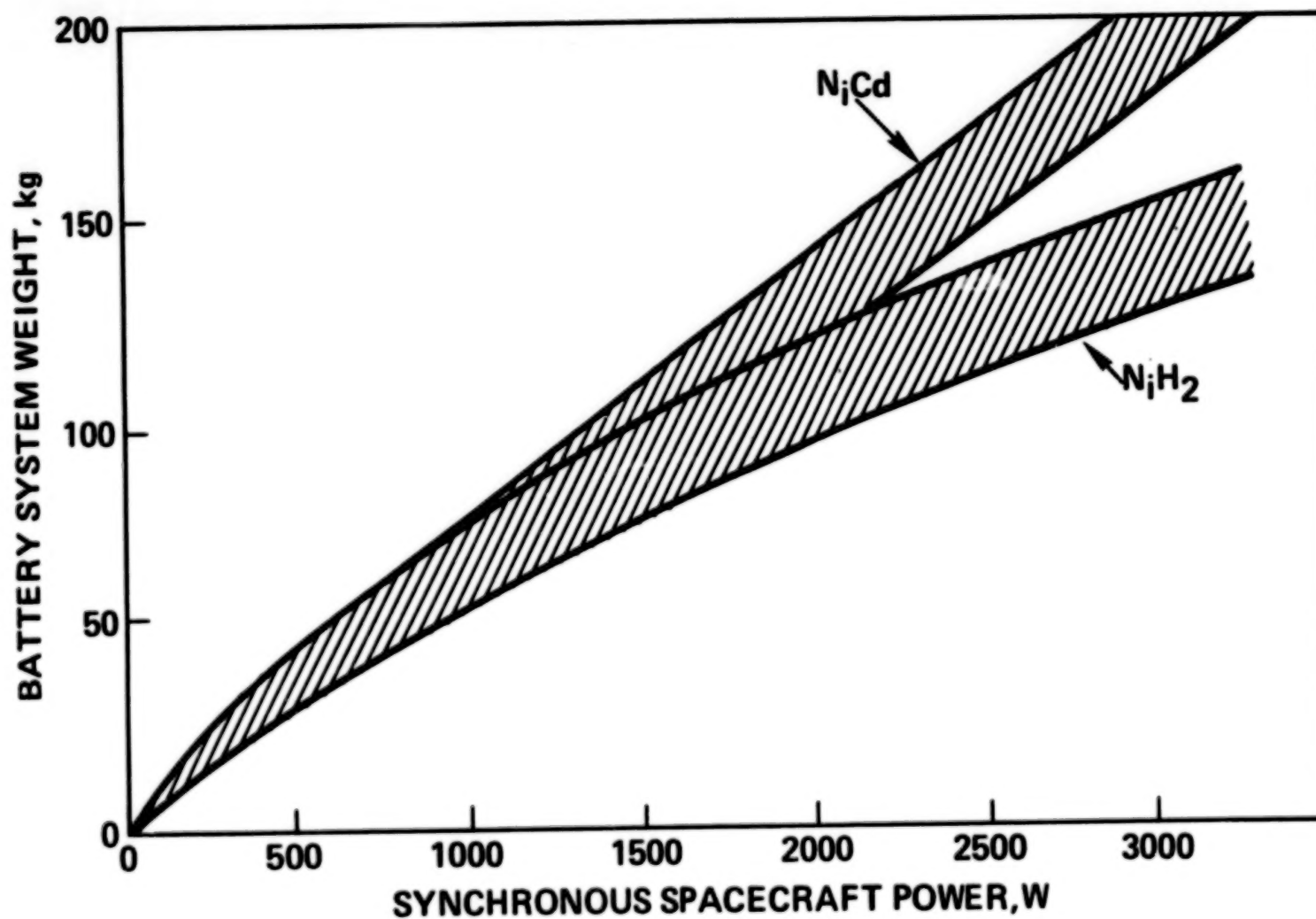
NICKEL-HYDROGEN BATTERY CELL
40 AMPERE HOURS



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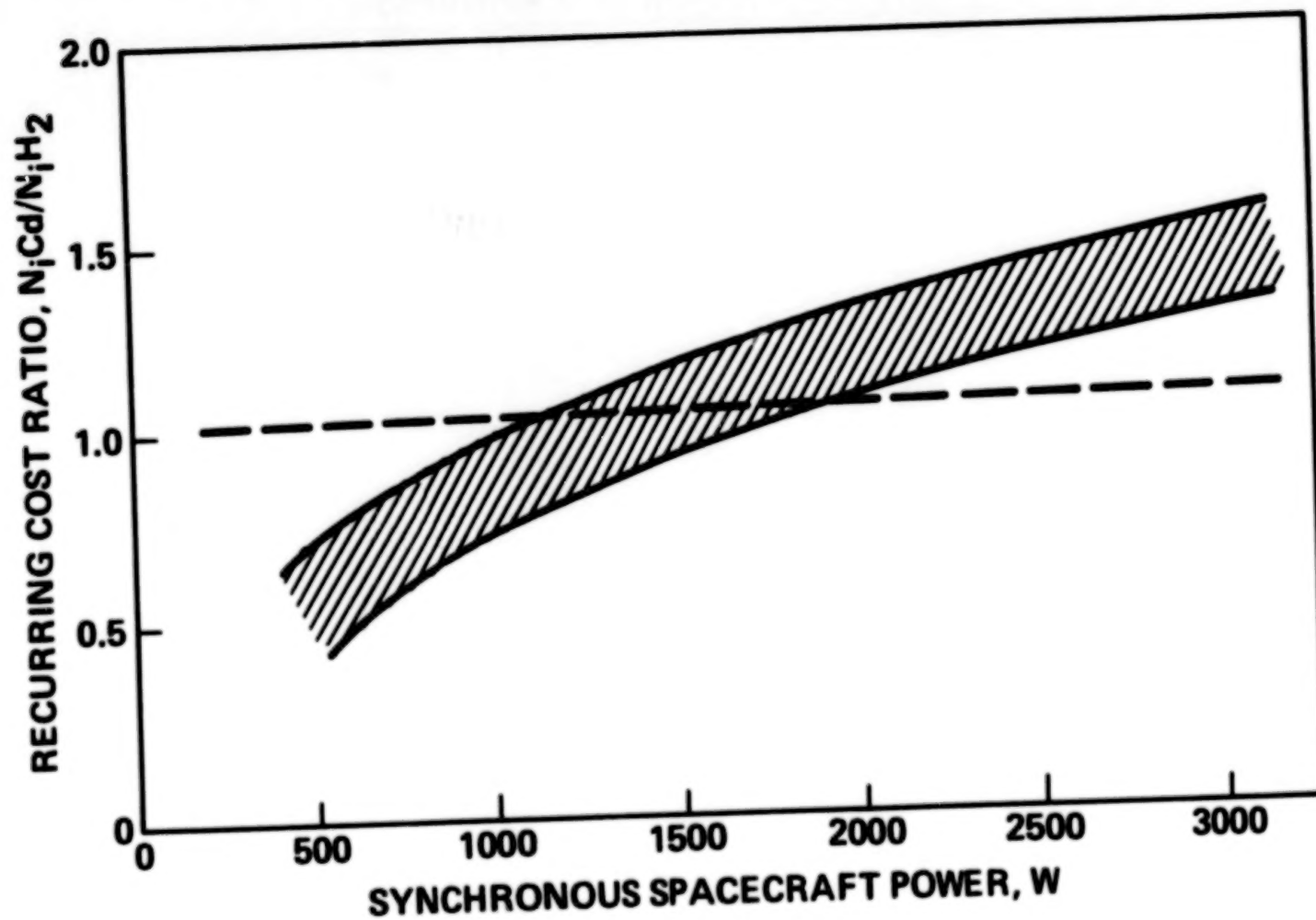


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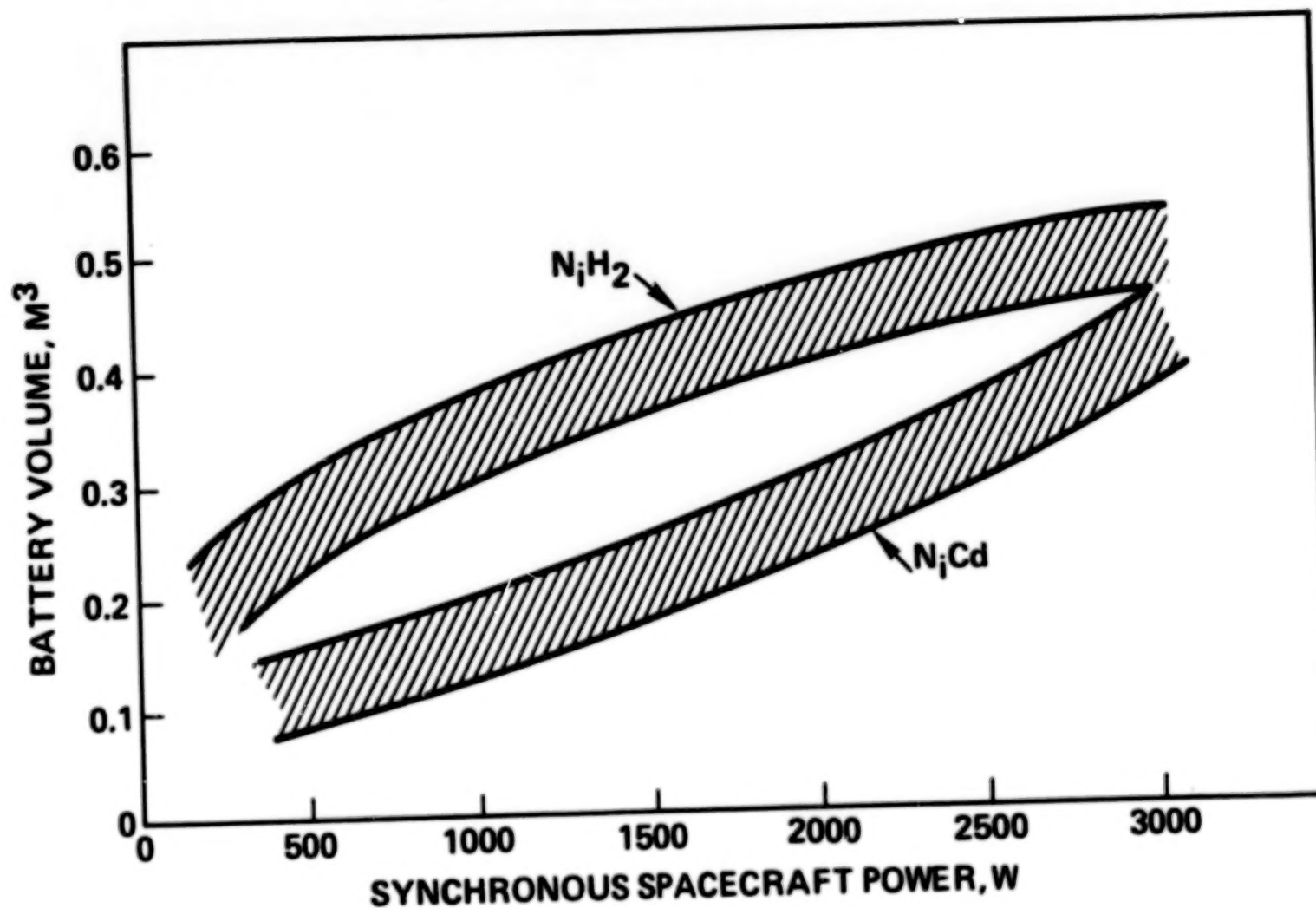
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CANADIAN EXPERIENCE WITH NICKEL CADMIUM SYSTEMS

by

J. L. Lackner

**Defense Research Establishment Ottawa
Ottawa, Ontario
K1A 0Z4**

November 1982

CANADIAN EXPERIENCE WITH NICKEL CADMIUM SYSTEMS

The Defense Research Establishment Ottawa (DREO) has been studying the nickel-cadmium system, both vented and sealed, since the early 1950's. Reasonable success has been achieved in a wide variety of applications covering: military vehicle use under Arctic conditions; high performance military aircraft; manpacked communications sets; remote standby power and small portable instrumentation. Our early studies on the vented system for high rate vehicle and aircraft cranking applications proved useful in our later studies on the sealed Ni-Cd system. This was especially true in the areas of plate loading and electrolyte composition. To achieve high rate cranking currents of 20C to 30C, it was necessary to have light to moderate plate loadings, a large reactive surface area, and electrolyte of optimum conductivity. These characteristics are very similar to the design required for sealed cells to insure good recombination rates. Our work on remote standby power and emergency lighting gave us an insight into the problems of "memory effect" and the need for periodic reconditioning.

DREO's involvement with spacecraft power systems dates back over 20 years to the launch of Alouette I on September 29, 1962. Research and development studies were conducted on cell components and manufacturing quality control. Some of our findings on electrolyte composition, separator optimization, power management, and recondition techniques have been reported over the years.

DREO has provided consultation to the Communications Research Centre/Department of Communications (CRC/DOC) and its predecessor, the Defense Research Telecommunications Establishment on the specification, qualification, and integration of sealed nickel-cadmium batteries for the Alouette and ISIS series of scientific satellites.

All of these spacecraft have successfully met and exceeded their mission requirements, attaining an average useful life of ten years in space. The ISIS I and ISIS II spacecraft are still operating after 13 3/4 years and 11 1/2 years respectively. It is interesting to note that this long life was obtained using "OLD 1960's" technology.

It became apparent at an early stage of our studies that although the nickel-cadmium system theoretically had many desirable characteristics, it was not always possible to obtain these desirable characteristics due to limitations in commercial manufacture at the time (1960).

As a consequence, DREO undertook some fundamental studies to understand the system from the inside out rather than test cells from the outside and then analyze their components. The conclusions of our studies were incorporated into our "Procurement Specification for Ni-Cd cells ISISA Spec S615-P-2".

A brief comment will be made on our choice of cell design and how some of the factors of cell manufacture could affect cell performance. If we consider some of this information from a historical aspect, we might be able to relate some inconsistencies in early test results with problem areas encountered in early cell design.

Substrate

The plate substrate chosen was pure nickel wire mesh to allow for flexibility in the jelly-roll cylindrical cell. Experience showed that iron wire or nickel plated wire was prone to ferric ion contamination.

Sinter

The loose powder sinter was chosen because at that time (early '60's) it had a better plaque porosity and more uniform pore size distribution. Blistering and shedding were common problems with early designs of perforated substrate and slurry sinter. Controlled pre-stressing of the plates and coining of the edges circumvented loose particle shorts. Today perforated nickel sheet and slurry sinter may be as good and possibly better, due to eliminating the possibility of wire shorts.

Impregnation

The plates were impregnated by chemical impregnation in small controlled lots. Unfortunately, the electrochemically impregnated plate was not available at this time. The plates were lightly loaded to maximize the reactive surface area for efficient recombination. The light loading also minimized the plate swelling and allowed for slightly more electrolyte volume. All plates were given at least five formation cycles to thoroughly convert all the active material and reduce nitrate impurities.

Assembly

Plates were characterized individually and selected on the basis of uniform weight gain, low nitrate content, and uniform capacity based on three open vat charge-discharge cycles.

It was necessary to match plates on both weight gain and achieved electrical capacity because plates selected on weight gain alone often showed inconsistencies in utilization of active material. To ensure good utilization, the raw plaques should be chemically clean and be within optimum limits of 75 percent to 85 percent total porosity. The pores have to be of sufficient size to allow the active material in and reasonably uniform throughout the plaque. This has a marked effect on current density and plate stress during cycling.

Electrolyte

Thirty percent KOH with less than 1 percent K_2CO_3 was specified. Following high temperature (40°C) cycling, the cells were checked to see that the carbonate level stayed below 3 percent. Impregnation and plate processing were done rapidly and inactive plates were always under N_2 atmosphere to minimize carbonate buildup.

The electrolyte was so selected to give maximum conductivity, minimum freezing the point, and the lowest solubility rate for cadmium. These criteria are supported by the findings of JPL and NWSC accelerated test results reported in the 1978 GSFC Workshop. High carbonate levels increase cadmium solubility, thereby encouraging cadmium migration and capacity fading. The sources of carbonate are attributable to: atmospheric contamination during processing, degradation of nylon separator, and impure electrolyte on initial filling.

Separator

Details of DREO separator studies are reported in a paper entitled "Q.C. Procedures and Measurements Polypropylene Separators for Sealed Ni-Cd Batteries" presented at Symposium on Battery Separators, ECS, Columbus, Ohio, February 18, 1970. DREO studies showed that polypropylene was superior to nylon in chemical resistance to KOH, attack by oxidation and resistance to thermal decomposition. Although polypropylene had superior characteristics to nylon, it did have two bad faults. Polypropylene is basically hydrophobic, so has poor wettability and poor electrolyte absorption qualities which result in short cycle life. Special wetting agents and electrolyte filling techniques plus processing of the polypropylene to improve its air permeability and surface loft, resulted in a good long life separator. The choice of polypropylene effectively minimized the buildup of carbonate in the cell due to separator degradation. We never saw any evidence of increasing negative capacity or hydrogen generation that was noted in some cells using nylon separator.

Seals

A Sonotone triple seal was used having a ceramic to metal seal sandwiched between two glass-to-metal seals. Because the original seals were difficult to manufacture and are no longer available, DREO undertook a seal technology study with the Ontario Research Foundation (ORF) to separate the art from the science of sealing.

Many of the early spacecraft seal designs were adaptations from the electronic industry and were not compatible with the chemical, mechanical, and thermal stresses of a nickel cadmium cell. Some early seal designs used silver brazes which quickly produced cell shorts.

ORF have now developed a Glass-Ceramic plug seal that is superior to the triple seal. This seal is reasonably economical and easy to manufacture.

There are several good seal designs available today, notably the G.E. hi-rel seal with nickel and gold braze. Sealing should no longer be a problem.

Cylindrical Can

The cylindrical can was selected because it was a natural pressure vessel. However, the jelly-roll design does present many assembly problems which the present day prismatic cell could overcome.

Total Spacecraft Power Concept

Even the best spacecraft battery can have difficulties if the total spacecraft power package is not fully integrated to ensure long life and efficient operation.

Historical Development Of Present Day Designs

Some of the problems associated with early spacecraft cells may be attributed to the fact that the plate material came essentially from the standard consumer cell production line which was not as demanding in quality as the aerospace cell required. Studies were undertaken by NASA/GSFC and various organizations to resolve the optimum design of spacecraft cells. Tyco Laboratories under contract to NASA/GSFC came up with a noteworthy study entitled "Development of Uniform and Predictable Battery Materials for Nickel-Cadmium Aerospace Cells" completed in late 1971. Unfortunately, problems associated with proprietary rights and the economic viability of the small aerospace battery market frustrated the commercial realization of this noble effort to characterize an ultimate Ni-Cd aerospace cell.

In recent years the needs of the military and consumer markets have coincided with those of the spacecraft industry, so that the major battery manufacturers could justify special attention to producing good aerospace quality cells. In particular, the demands for high rate aircraft batteries, small portable consumer appliances, and the needs of the computer industry has created a need for high quality plate material.

Many of the desirable features of spacecraft cell design are now being incorporated into these applications, namely: polypropylene separator, light loading, electrolyte parity, improved seals and high reactive surface area. Examples of such commercial products are: G.E. Gold Top cells, G.E. 15 VP cells and Marathon Low Stress cells.

The sealed nickel-cadmium cell thrives on activity and degrades when it is left on open circuit or low rate trickle for extended periods of time. Flight and test experience has shown that batteries in LEO spacecraft tend to have longer lives than under-utilized batteries in geosynchronous orbits. Regular use of the battery and periodic reconditioning is a necessity.

To minimize the stress of excessive overcharge, charge at rates up to C/3 for maximum efficiency and minimum C/D ratio.

The Nickel Cadmium Cell Today

The past ten years have seen some major advances in improving the reliability of the Ni-Cd cell. There was a major breakthrough in early 1970 when Maurer and Beauchamp of Bell Laboratories introduced their electrochemically impregnated plates - several variations of E.I. plates are available now. The E.I. process should be the best method available today. It should increase the energy density by a factor of two, minimize plate swelling, increase electrolyte volume, and give better plate uniformity.

The development of the NASA High Reliability specification and Standard Cell Program have improved the uniformity of production.

The nickel-cadmium cell today can be considered to be a mature product. There is a wealth of reference material available on theoretical studies, accelerated testing, and flight proven data. We can thank GSFC for having made it possible to generate and exchange much of this technical information. In fact, GSFC even put out a Bibliography of Reference Material and an Applications Manual to assist us.

The fact that most of the main manufacturers have a viable consumer market for sealed nickel-cadmium cells is promising. Both the aerospace industry and the consumer benefit from the continuing development of the product.

Summary

Although the Ni-Cd battery may have some annoying short comings with respect to the negative plate and the separator, there is enough information available both publicly and privately to specify, design, manufacture and critically test a viable Ni-Cd spacecraft battery to last a minimum of five years. With reasonable care and attention a ten year design is possible right now.

The flexibility of the Ni-Cd system allows us to design deep DOD batteries for short to medium life missions or moderate DOD batteries for long life. However, it is debatable if we can design a high DOD, long life, light weight, high energy density Ni-Cd battery. There are limitations to the system and we should recognize them, not compromise them. Weight savings and high energy density are desirable goals provided they do not compromise reliability. The weight of the battery on most spacecraft represents 6 percent to 10 percent of the total weight, so it is not a major weight contributor.

The present day Ni-Cd technology is adequate for spacecraft designs up to 1.5 kw power levels and may be even up to 3 kw power levels. Beyond 3 kw a better energy density system is desirable. We should look for something that will be better by several orders of magnitude to justify the problems associated in qualifying a new system.

DREO PAST ACCOMPLISHMENTS

1. PROVIDED CONSULTATION TO CRC/DOC

ALOUETTE 1	ISIS 1
ALOUETTE 2	ISIS 2

2. R&D ON NI-CD CELLS & COMPONENTS

ELECTROLYTE PURITY

SEPARATOR OPTIMIZATION

GLASS & CERAMIC TO METAL HERMETIC SEALS

IMPREGNATION STUDIES

POWER MANAGEMENT & RECONDITION TECHNIQUES

WELDING TECHNIQUES

FAILURE ANALYSIS

BEST DOCUMENT AVAILABLE

DREO PAST ACCOMPLISHMENTS

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POWER MANAGEMENT & RECONDITION TECHNIQUES

WELDING TECHNIQUES

FAILURE ANALYSIS

SPACE CRAFT DATA

	<u>ALOUETTE 1</u>	<u>ALOUETTE 2</u>	<u>ISIS 1</u>	<u>ISIS 2</u>
LAUNCH:	29SEPT62	29NOV65	30JAN69	31MAR71
LIFE:	30SEPT72 10 YRS	1AUG75 9 2/3 YRS	STILL 13 3/4 YRS	OPERATING 11 YRS 7 MOS
CELL:	All cylindrical - sonotone			
CAPACITY-AHRS:	6	6	8.5	8.5
CHARGE MODE:	All c/10			
SEPARATOR:	Polypropylene			
ELECTROLYTE:	30% KOH 3.0% K_2CO_3			
ORBIT:	LEO			
PLATE LOADING:	Light to moderate			
NEG: POS PLATE RATIO:	1.7:1 min 2.0: 1 max			
DOD:	15% to 45%			

FACTORS AFFECTING CELL MANUFACTURE

1. Substrate: Wire mesh perforated sheet
2. Sintering Method: Slurry SAFT process loose powder sonotone
3. Impregnation: Fleisher Chemical, Bell Electrochemical
4. Formation Cycles and Process Controls.
5. Assembly - necessity for special aerospace line
6. Electrolyte: Conc., Purity, Volume
7. Separator: Nylon or Polypropylene
8. Seals
9. Can and Welds.
10. Cylindrical or Prismatic.

THEORETICALLY ACHIEVABLE
CHARACTERISTICS OF
NICKEL CADMIUM SYSTEM

Good Cycle Life: Up to 50,000 cycles

Long Life: 10 to 30 years

Rapid Recharge: $C/3$ to C rate

Wide Temperature Range: -40°C to 50°C

High Rate Discharge: 3C to 10C

Low Internal Resistance: 3 to 10 m Ω /cell

Good Storage Life: 10 years

Rugged:

Moderate Cost:

Low Pressure Device: 10psi - 75psi

Flexible Design: 100mah to 50Ahr

Easy Packaging of Prismatic Construction: Good Thermal and Mechanical Interface.

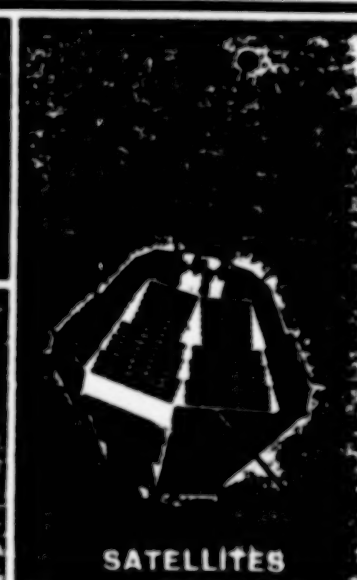
RECHARGEABLE SINTERED-PLATE, NICKEL-CADMIUM BATTERIES power for...



TOOTHBRUSHES



CORDLESS KNIVES



SATELLITES



JETS

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General Electric's
PowerUp-15[®]
rechargeable
nickel-cadmium
battery

RECHARGES TO 95% CAPACITY IN ONLY 15 MINUTES

- o Reliable, economical 15-minute charge system
- o Capable of repetitive fast charge cycling
- o All the advantages of time-proved GE nickel-cadmium rechargeable batteries

*Trademark of General Electric Company



GENERAL ● ELECTRIC

OTHER PRESENTATIONS

EXPERIMENT DESIGN

H. Lim, Hughes Research Laboratory

DETERMINATION OF THE RELIABILITY OF Ni-Cd BATTERIES FROM SURVIVAL DATA ON CELLS FABRICATED 1964-1977.

A.S. Jordan and T.D. O'Sullivan, Bell Laboratories

TBS

F. Perez, Hughes Aircraft Company

TEST METHODS AND RESULTS OF THE 10-CELL BIPOLAR NICKEL HYDROGEN BATTERY

R. Cataldo, NASA/Lewis Research Center

EXPERIMENTAL DESIGN

by Lim

Nickel Electrodes

Before going into my topic, I would like to take a few moments to comment on and give you a background of my program. We have interest in both areas. We have two programs; one is trying to make long life, low weight nickel cadmium cells. Also, we are working on a NASA program to optimize nickel electrodes for the best performance, especially for long life, which I am going to talk about. This is going to be a status report rather than the final one. Our experience is based on the component level, especially the polar plate cells. The only thing I would like to point out is when the components are compared with the same components, we think both the nickel cadmium and the nickel hydrogen life is limited by the nickel electrode wearout rather than anything else. We have published three papers on these subjects which have lasted two years. Last year was the IECE conference and this year the Battery Conference. Let me remind you of some of the results. We have achieved even conventional nickel electrode and we have advanced the organic separator. Right now we have over 33,000 cycles at 40% DOD. This is a fast modified electrottype cycle. Another one is at 80% DOD and we have achieved around 8,000 cycles today.

My talk today is long life nickel electrode for nickel hydrogen cell. This may not contribute to the questions today, but we have some efforts to optimize the nickel electrode for long life, especially in terms of the pore size variation of the plaque and mechanical strengths and active material loading.

It took us three levels of the experimental parameters [Figure 1] changing the mechanical strengths and the pore size of the plaque in three levels and active material loading. The mid-level is roughly the standard level for the standard electrode for Hughes Aircraft--nickel hydrogen electrodes. The higher level changes roughly 1% and of these two different parameters, and lower level is 10% lower than the standard level. The core size--we are trying to change the maximum variation without changing the basic dry center technique that we are using.

At this point, I would like to point out that the electrode fabrication work is done at (Earl Pitcher), Colorado Springs and most of the experimental data is taken by Carol Frazer. The general approach is that we make this electrode in three levels of a variation which you will have a total matrix of 27 and fabricate this and...we go through the initial stress to test eliminate by prescreening certain combination of electrodes. The stress test is made of 200 cycles. Then if the electrode passes the stress test, we are going to make a boiler plate cell

EXPERIMENTAL DESIGN

and go through the faster cycle life test and tear down analysis and based on this test we will recommend which electrode design is going to be the best electrode. Today I am going to talk about the progress of the stress test.

First, to select the pore size and mechanical strength we did some manufacturing studies. Basically, we changed the two parameters. One is powder type, including the powder density and centering time to change the flow characteristic. This is the relation between bending strength, pore size, and powder type, including the powder density for three different types of powders. [Figure 2] What we can see here is with each different type of powder, if we change the powder density, we change both pore size and bending strength.

Another type of data is we fixed the power type on individual curves and changed the conveyor belt speed [Figure 3]--with a constant profile, which is essentially changing the centering time. The interesting result is the bending strength depends on the net speed while the pore size is more or less constant. One thing we can choose is, we like to have the maximum pore range, which is roughly 10-16. As you can see, we cannot get the high strength of plaque. We are trying to vary from 400 to 700, so we end up with actually seven combinations with the lowest pore size of three combinations with three strengths.

This is the combination. We chose to make a 19 boiler plate cell. Which is shown here [Figure 4] by asterik. I am going to give you some of the plaque data. When we plot some relationships between various parameters [Figure 5], like porosity and bend strength, we have roughly straight lines. But only if the individual powders have a different porosity.

Another one is the hardness and bending strength [Figure 4]. We did not have a very good correlation between the bending strength and the hardness, but surprisingly we had hardness in the median pore size. We do not have a real explanation on that. Another is, we measure the surface area. Surface area only correlates with the centering time. We tried various other correlations, but we did not have a very good correlation with other parameters [Figure 7].

[Figure 8] There is some relationship between bending strength and resistivity. They have a good correlation and also porosity and resistivity have some correlation. This is not really the deciding factor for making the choice. When we prepare the seven different types of plaques to load in three different loadings, we had five different impregnation times.

EXPERIMENTAL DESIGN

[Figure 9] This is one of the typical curves and out of this excess number of plaques that were produced, we have taken 1.4 grams and put g/cc void and 1.55, which is the median loading, and 1.7. We have chosen the plaques and made the electrodes.

After making these electrodes, we have gone through these 200 cycle stress tests [Figure 10]. This one involves a one capacity measurement at a very high rate--5C charge and C rate discharge. And 200 stress cycles at 10C charge and discharge rate and then five capacities were measured. Then it was disassembled for visual inspection and metal thickness and weight. All this--the 21 electrodes were made, which is 3 X 7--passed the visual inspections. That means there is no severe blistering.

[Figure 11] You see the capacity changes. This a before and after stress test. One interesting thing is the before stress test looks like the capacity is not really stabilized. We tried to find some kind of correlation, so we plotted out the utilization, the measured capacity divided by theoretical capacity based on the loading. This is plotted against the active material loading. The data is scattered all over. That means that it is probably not stabilized. As seen [Figure 12], there is a definite trend that when the active material loading is increased, utilization is decreased.

[Figure 12] When we measure the weight decrease after the stress test, all the others except the 16 micro plaque have a little higher weight loss and all the others are indistinguishable. The electrode thickness shows there is a definite trend that the thickness is increased as the active material loading is increased. But again, the data is very scattered, which is probably because of the fact that the active material loading is calculated based on the big size plaque out of which we are making nine electrodes. If there is some local variation, we can expect some scattering. But the general trend is as the active material loading is increased, it increases the utilization.

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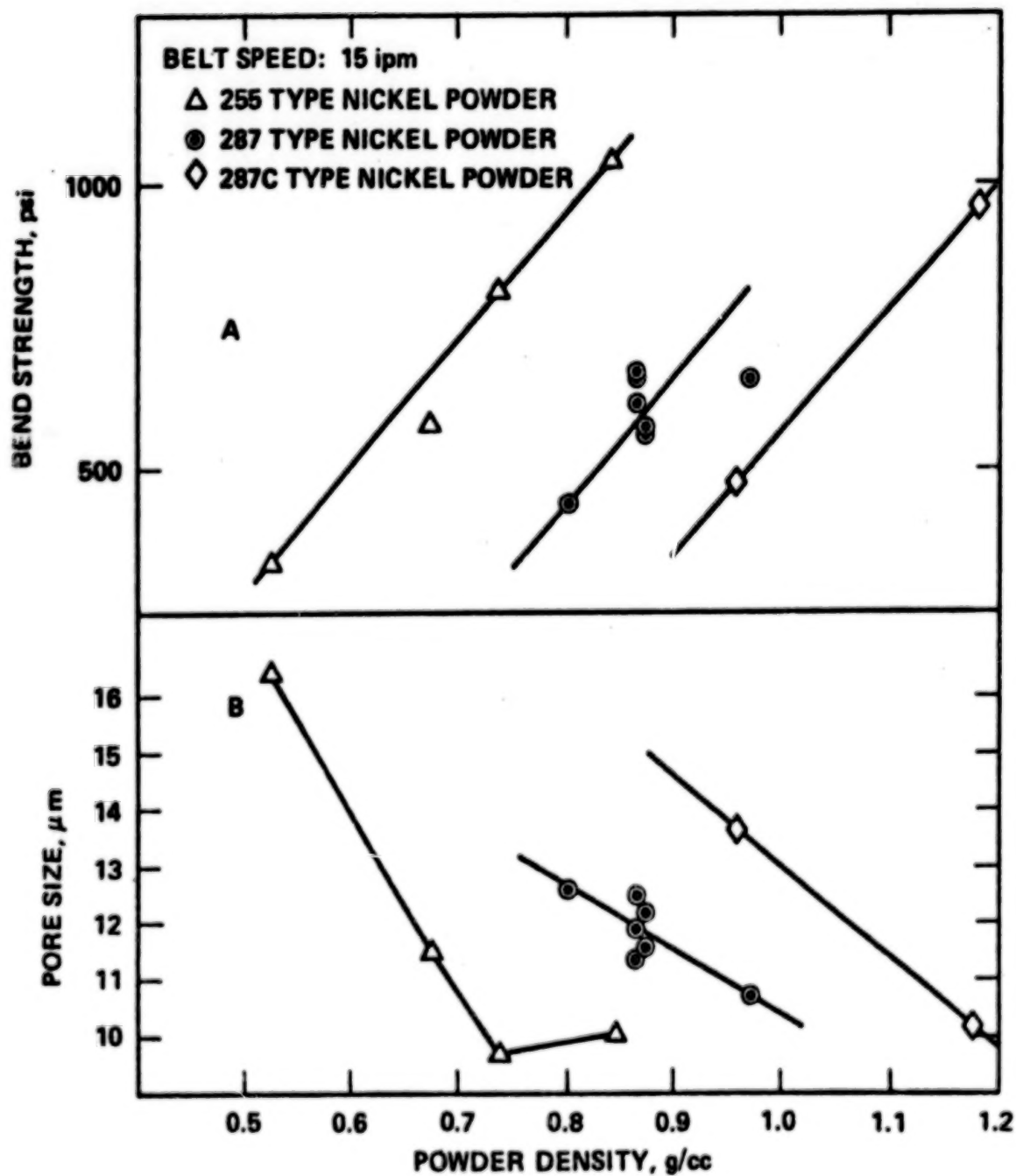
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EXPERIMENT DESIGN

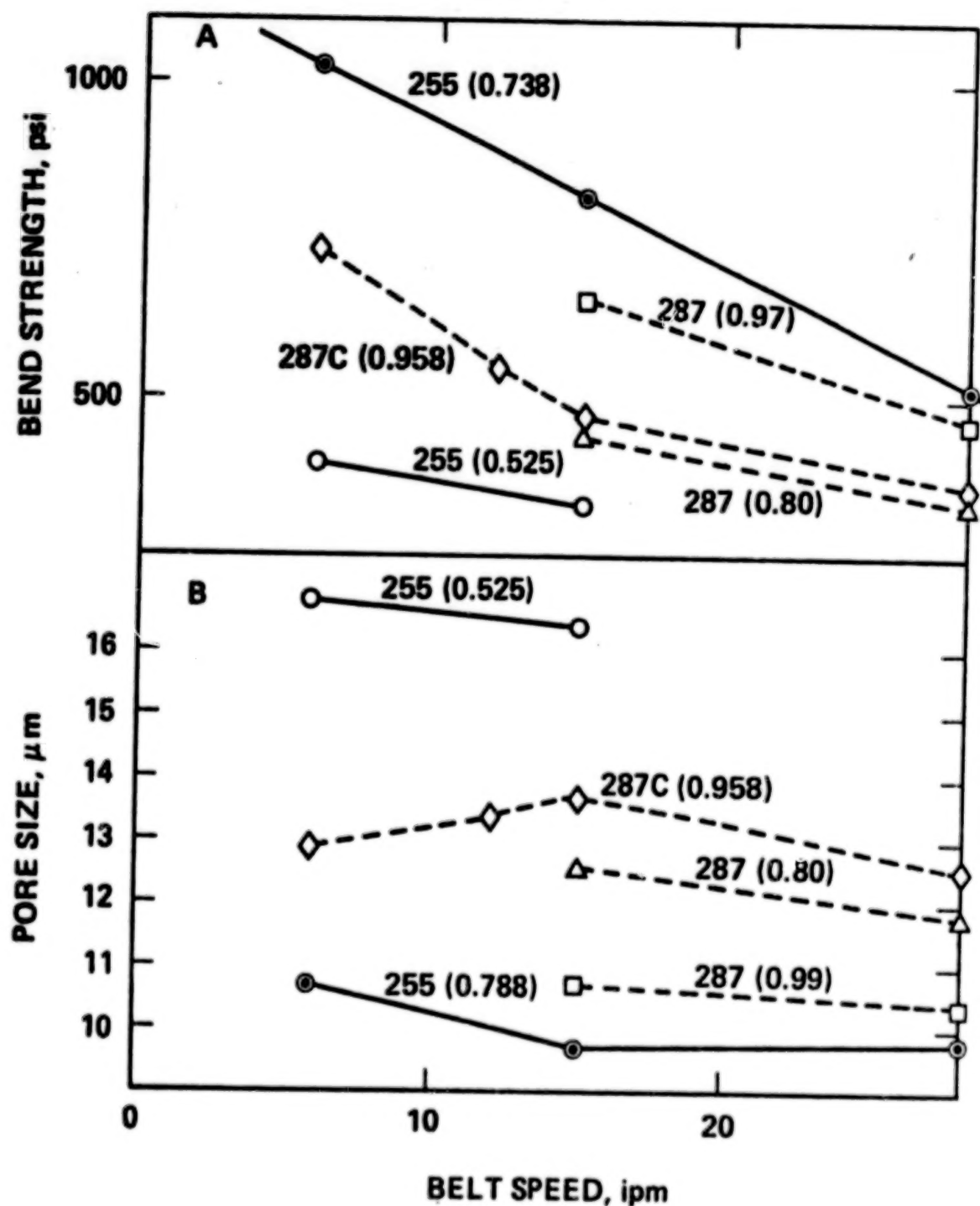
LEVELS	1	2	3
PLAQUE MECHANICAL STRENGTH (psi)	400	550	700
PLAQUE PORE SIZE (μ IN DIAMETER)	10	13	16
ACTIVE MATERIAL LOADING LEVEL (g/cc VOID)	1.4	1.55	1.7

PLAQUE BEND STRENGTH AND PORE SIZE vs POWDER DENSITY



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PLAQUE BEND STRENGTH AND PORE SIZE vs BELT SPEED



BOILER PLATE CELL TEST PLAN

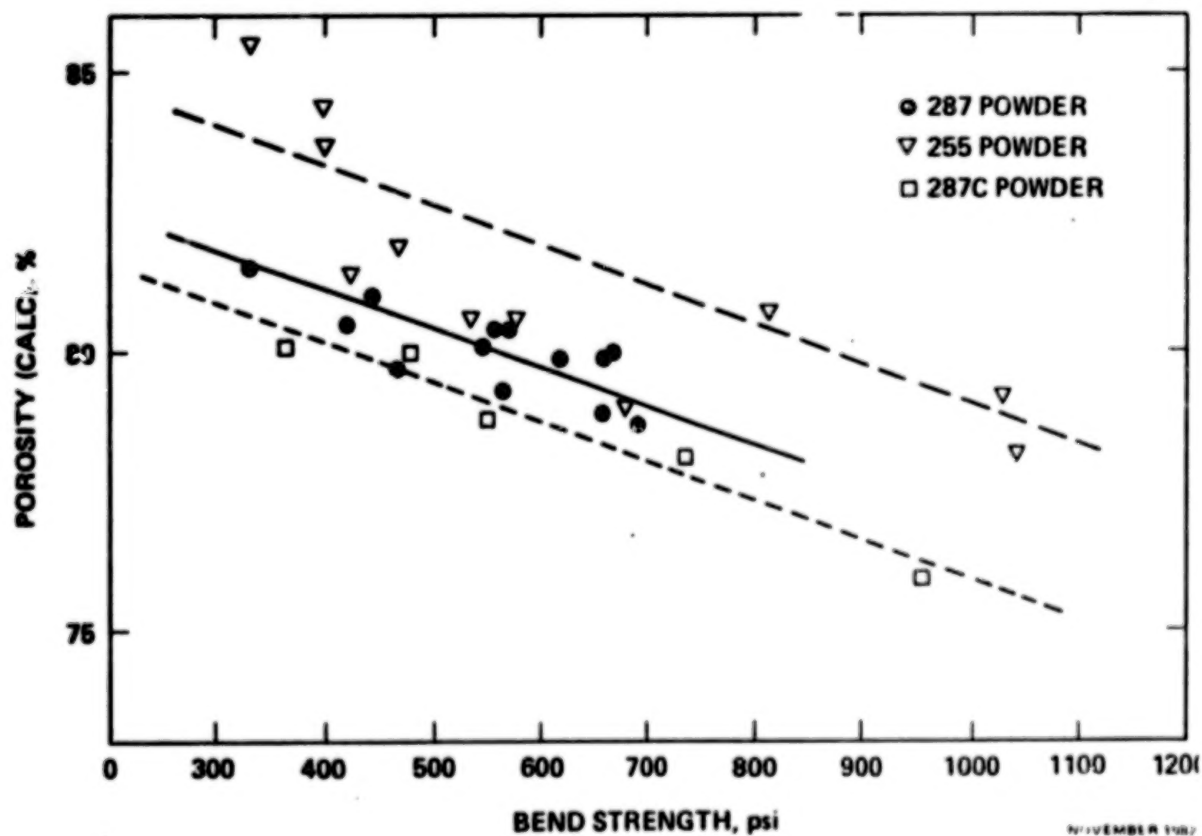
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BEND STRENGTH PORE SIZE, μm ACTIVE MATERIAL LOADING LEVEL	400 psi			550 psi			700 psi		
	10	13	16	10	13	16	10	13	16
1.4 g/cc VOID	*	*	*	*	*			*	
1.55 g/cc VOID	*	*	*	*	*		*	*	
1.7 g/cc VOID	*	*	*	*	*			*	

* INCLUDED IN TEST CELL MATRIX OF TOTAL 19 CELLS

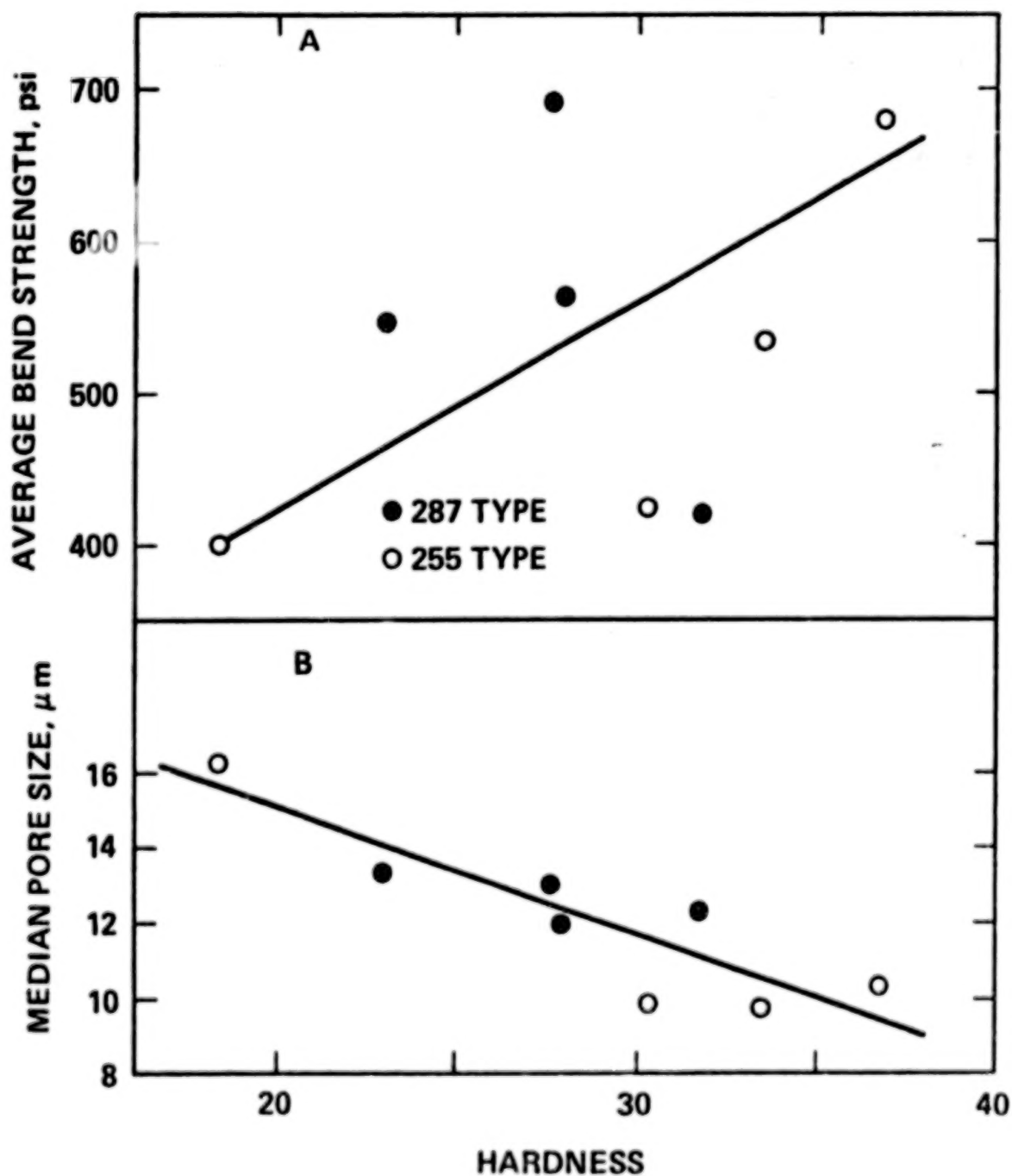
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PLOTS OF POROSITY (CALC) vs BEND STRENGTH

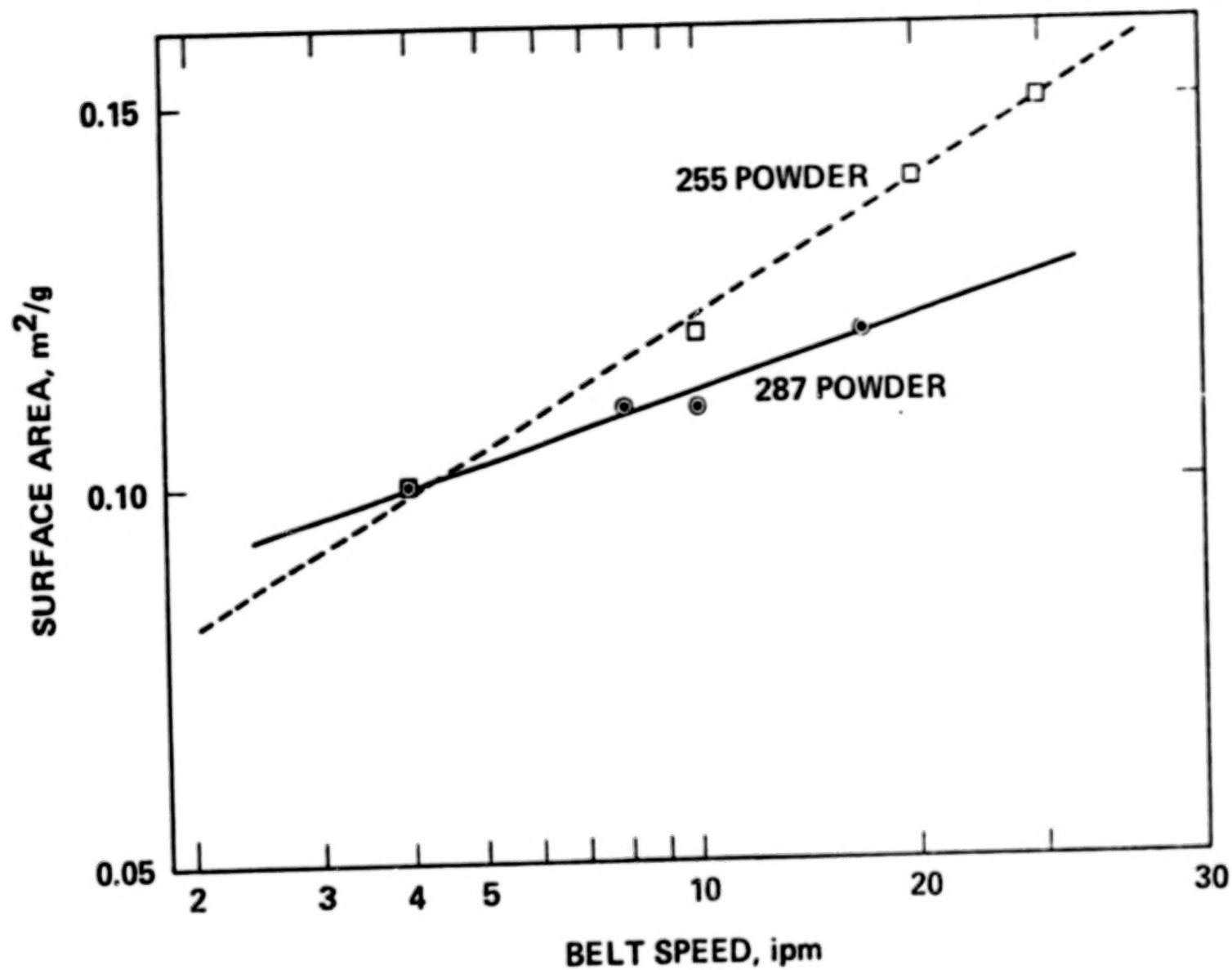


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**PLOTS OF AVERAGE
BEND STRENGTH AND
MEDIAN PORE SIZE
vs HARDNESS**



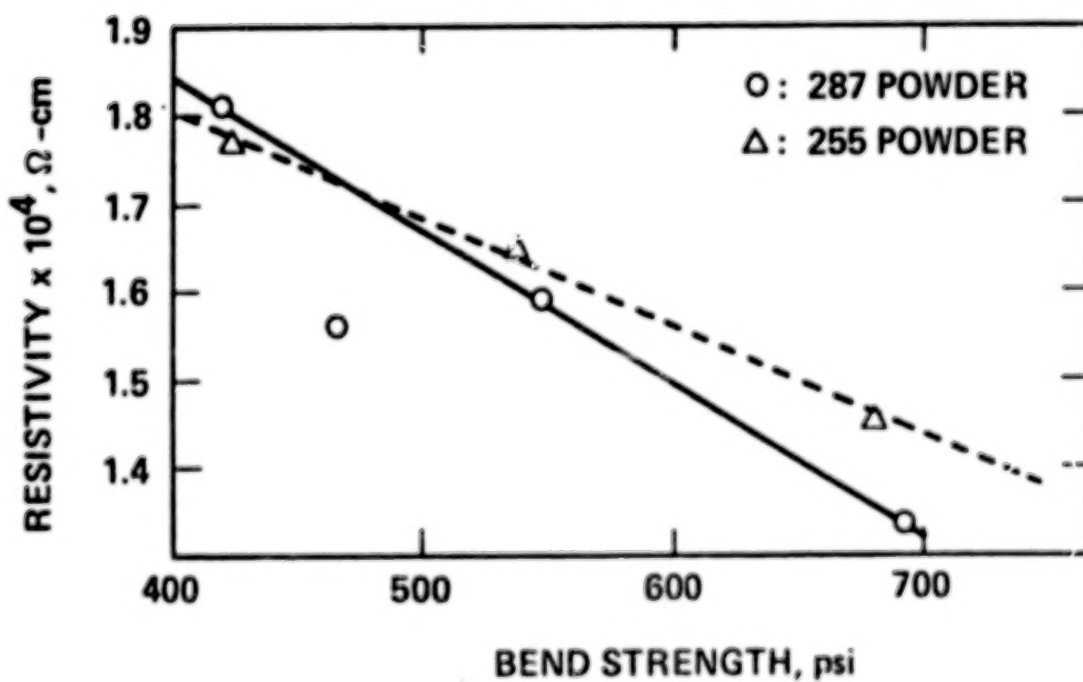
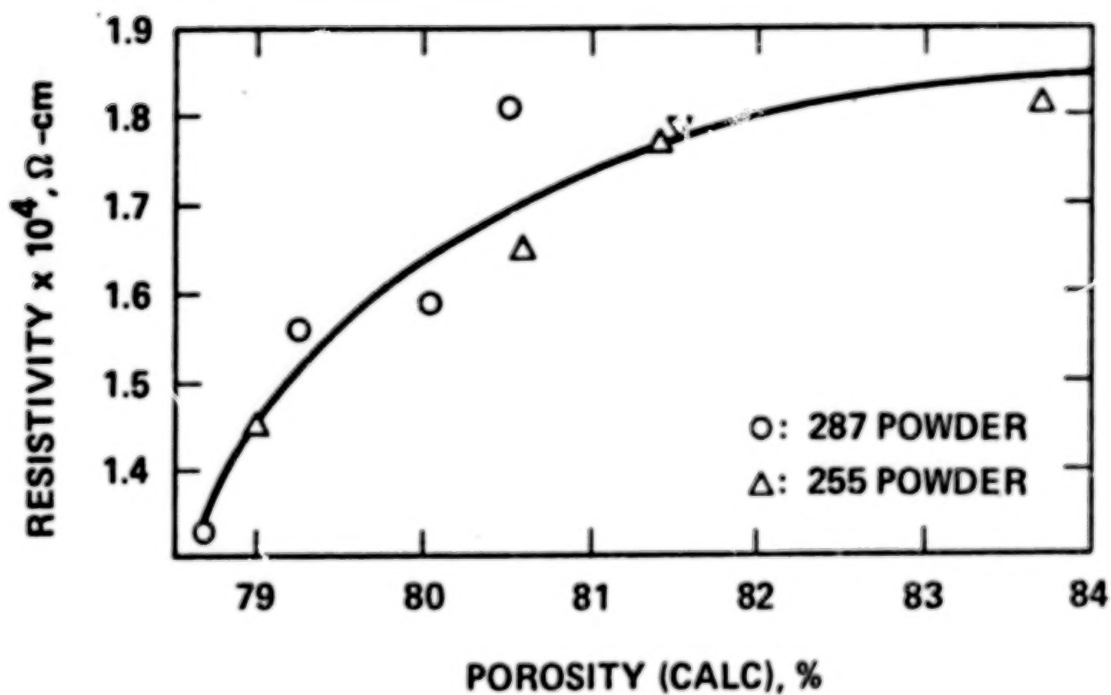
**PLOTS OF SURFACE AREA (BET METHOD) vs
BELT SPEED (INVERSE OF SINTERING TIME)**



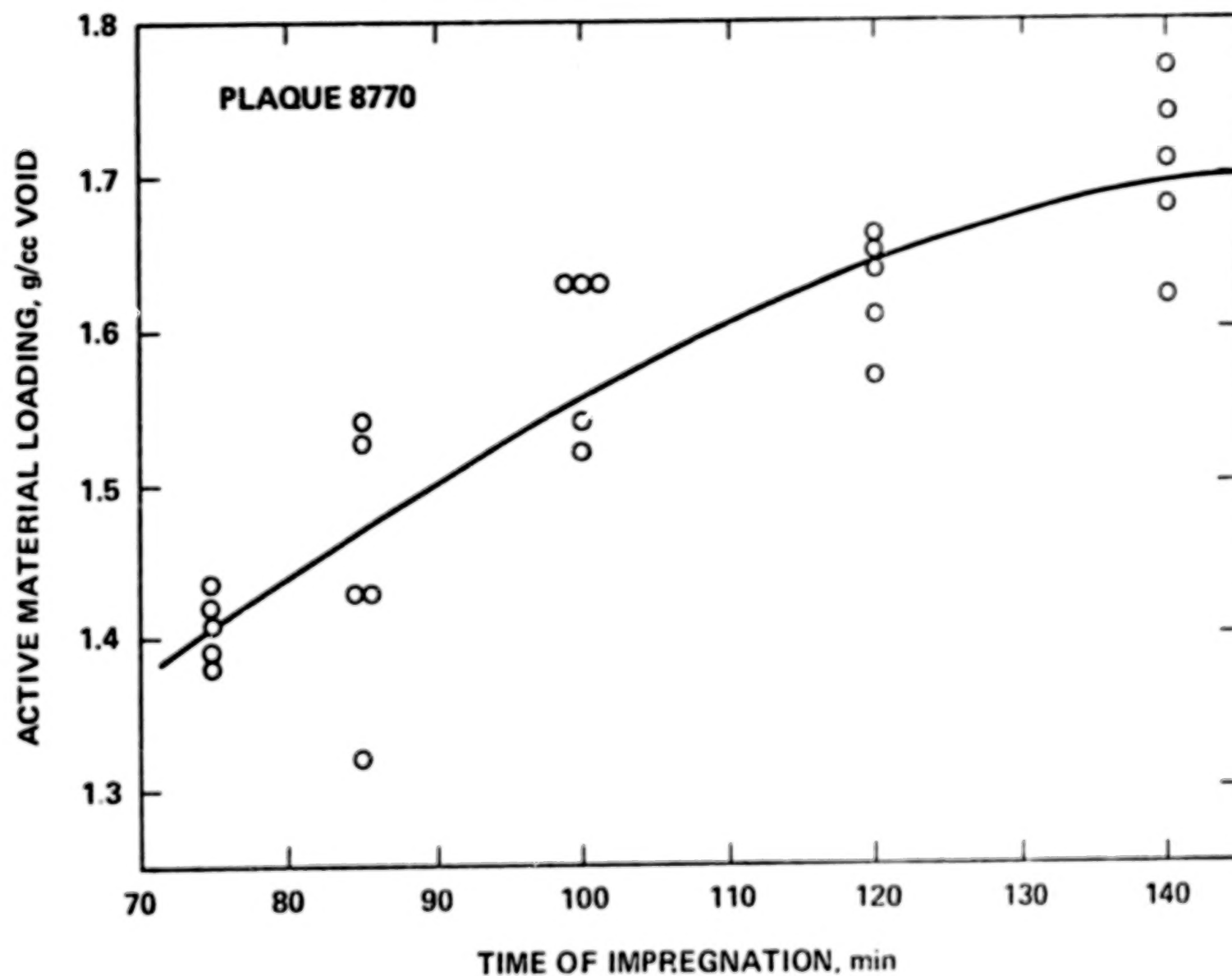
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PLOTS OF PLAQUE RESISTIVITY vs POROSITY AND vs BEND STRENGTH



A TYPICAL LOADING CURVE OF ACTIVE MATERIAL

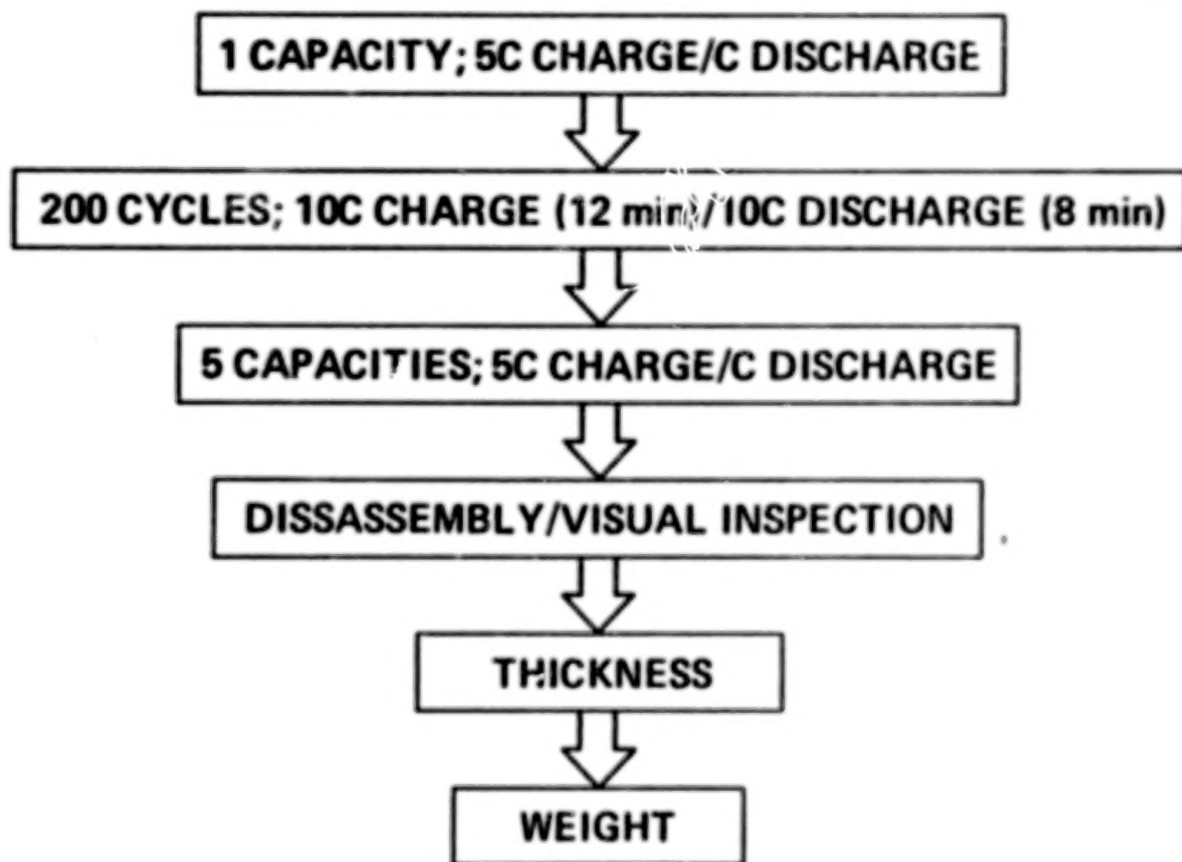


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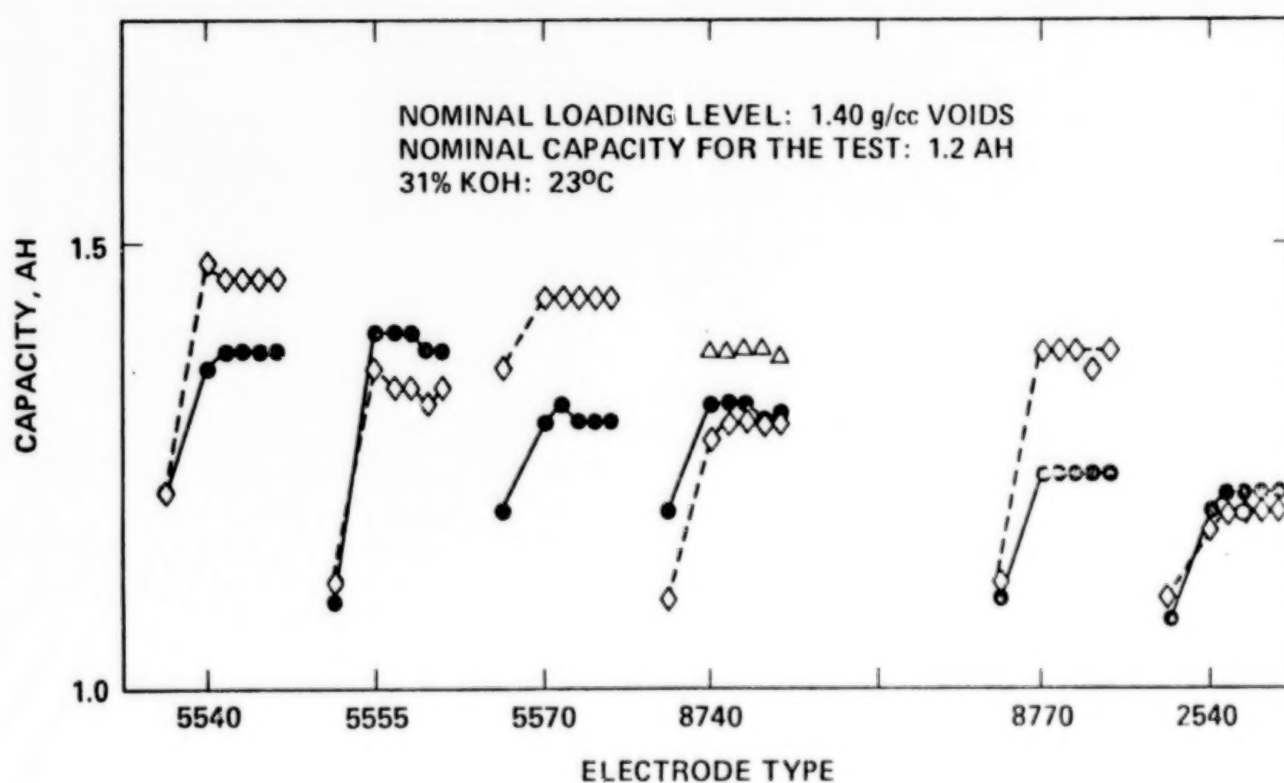
**A 200 CYCLE STRESS TEST OF NICKEL ELECTRODES
FLOODED 31 % KOH**

12452-1/2



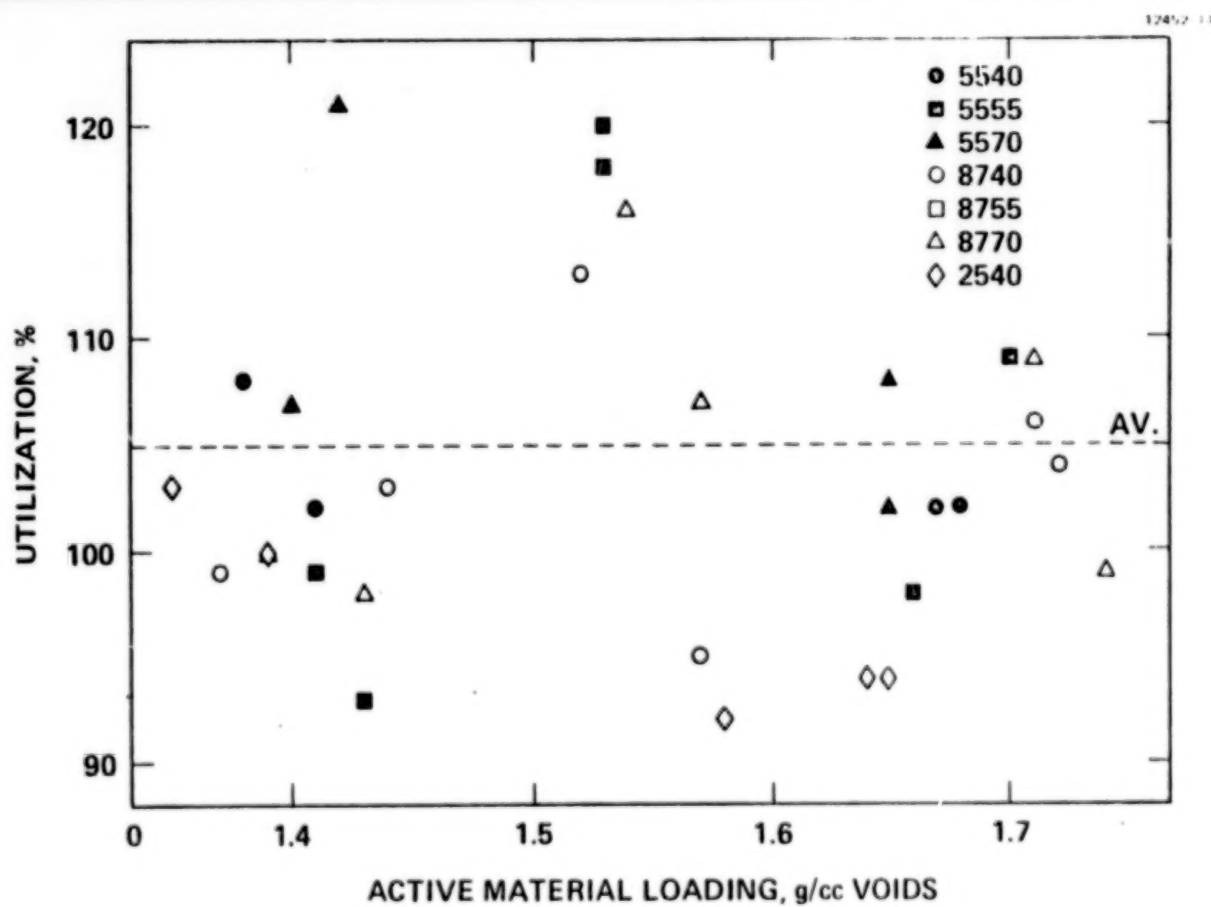
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TYPICAL NICKEL ELECTRODE CAPACITIES BEFORE AND AFTER STRESS TEST



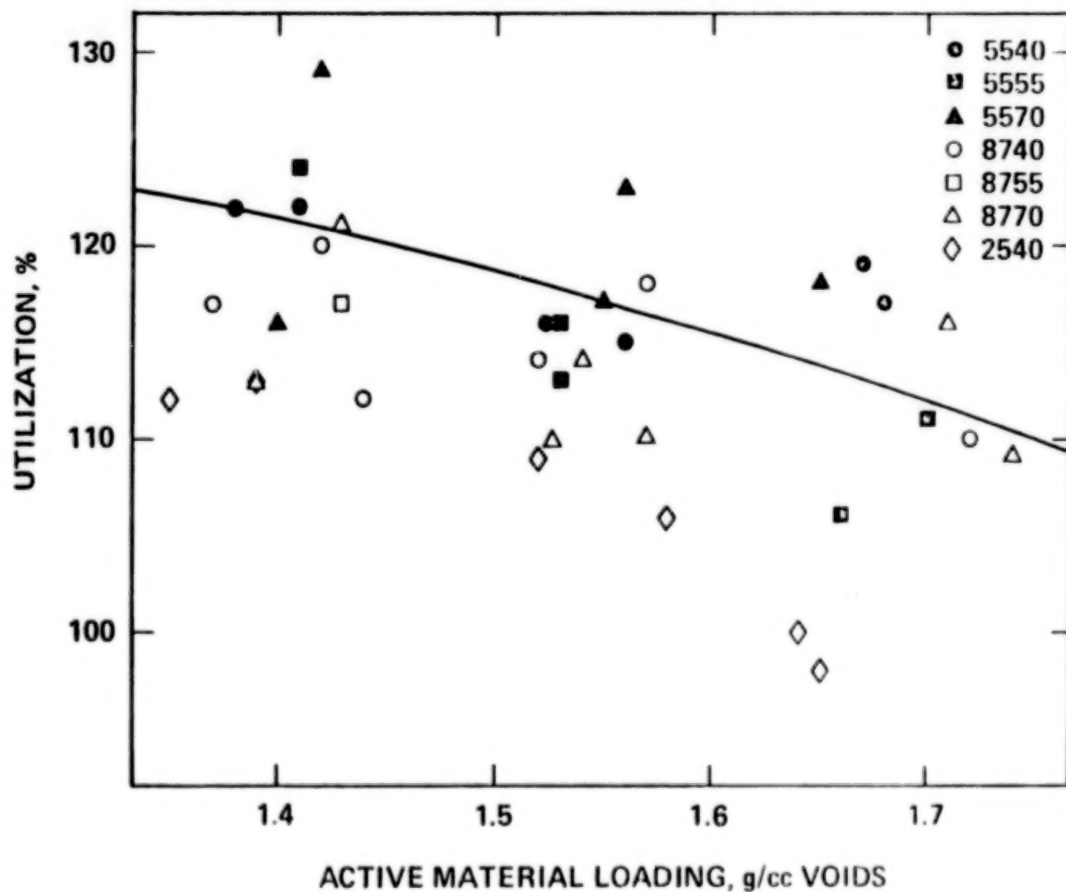
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ACTIVE MATERIAL UTILIZATION BEFORE STRESS TEST vs LOADING LEVEL



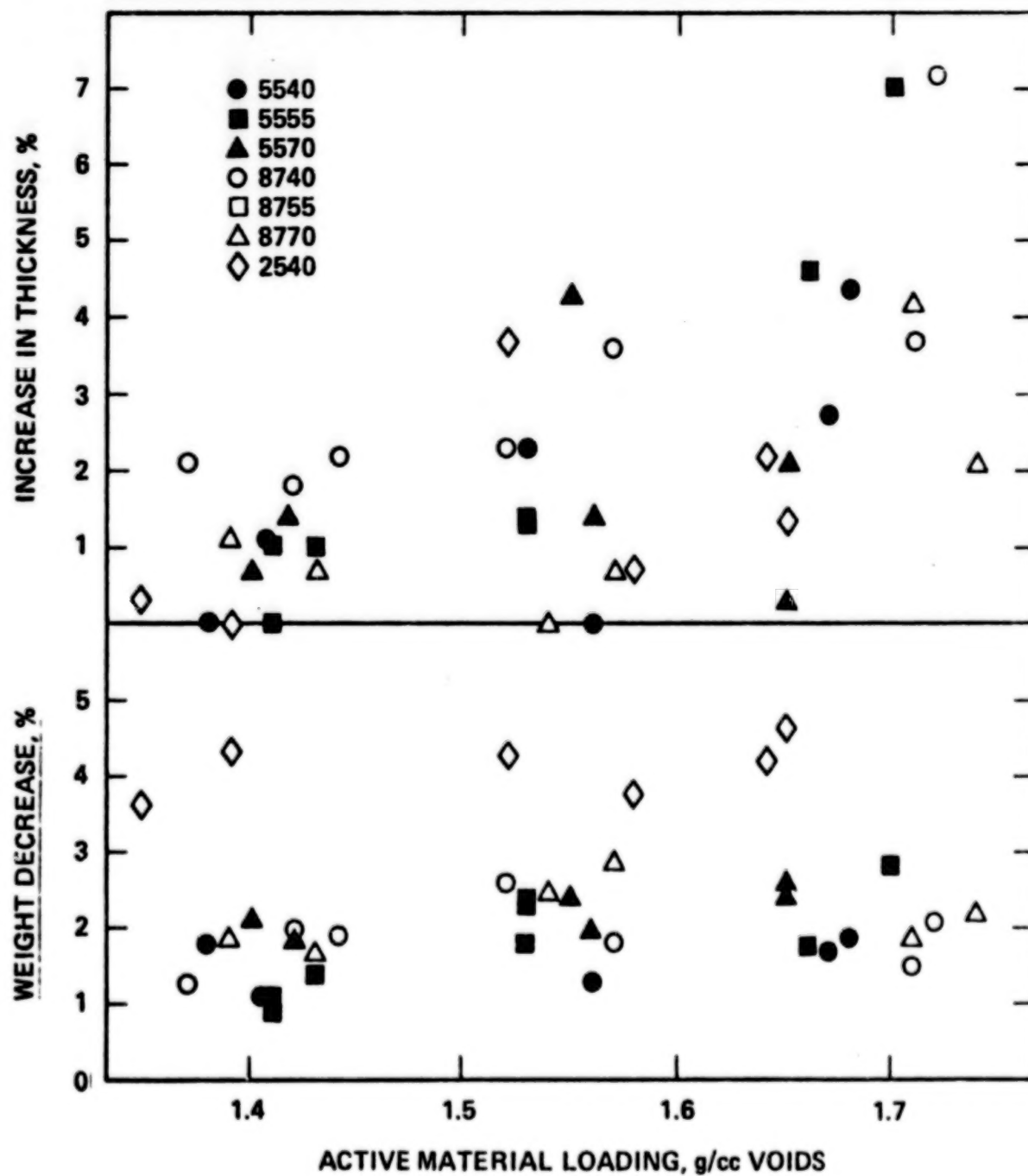
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ACTIVE MATERIAL UTILIZATION AFTER STRESS TEST vs LOADING LEVEL



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WEIGHT AND THICKNESS CHANGE OF NICKEL ELECTRODES AFTER STRESS TEST



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DETERMINATION OF THE RELIABILITY OF Ni-Cd BATTERIES
FROM SURVIVAL DATA ON CELLS FABRICATED 1964-1977

A. S. Jordan and T.D. O'Sullivan
Bell Laboratories
Murray Hill, New Jersey

DISCUSSION OUTLINE

- Statistical methodology: Log-normal distribution
- Crane real time tests on General Electric prismatic cells
- Low earth orbit 0° , 22.5° , and 40°C
- Geosynchronous orbit 0° and $22.5^{\circ}\text{C} - 11^{\circ}\text{C}$
- Battery survival probability

ANALYSIS PROCEDURE

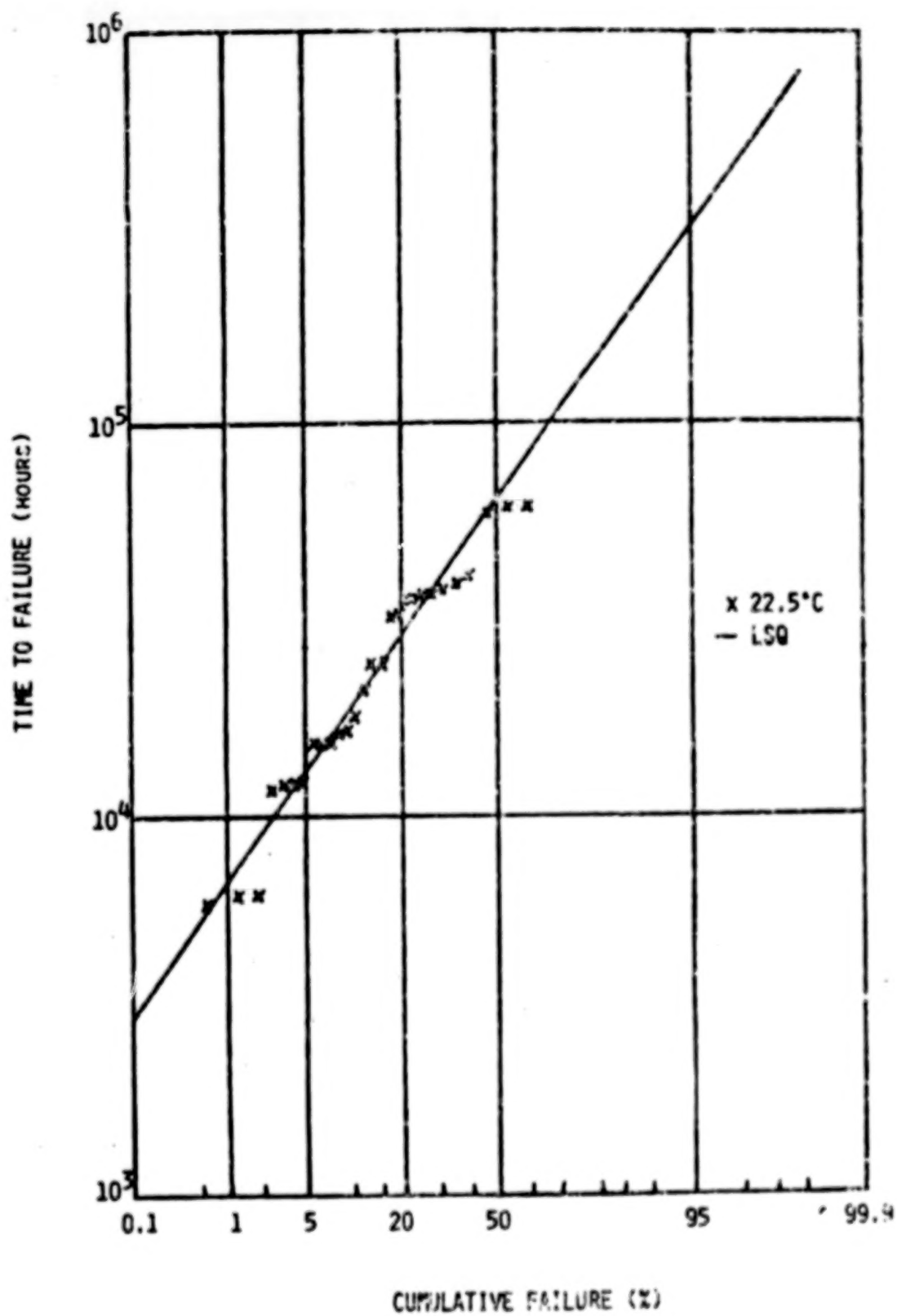
- Data base is Naval Weapons Support Center, Crane, Indiana. Tests are in 19th year.
- Log of cell failure times are plotted against cumulative failure percentage and mean and standard deviation determined.
- Terminations of cells are handled by method of Kaplan and Meier (Journal American Statistical Association, 53,457 (1958)).

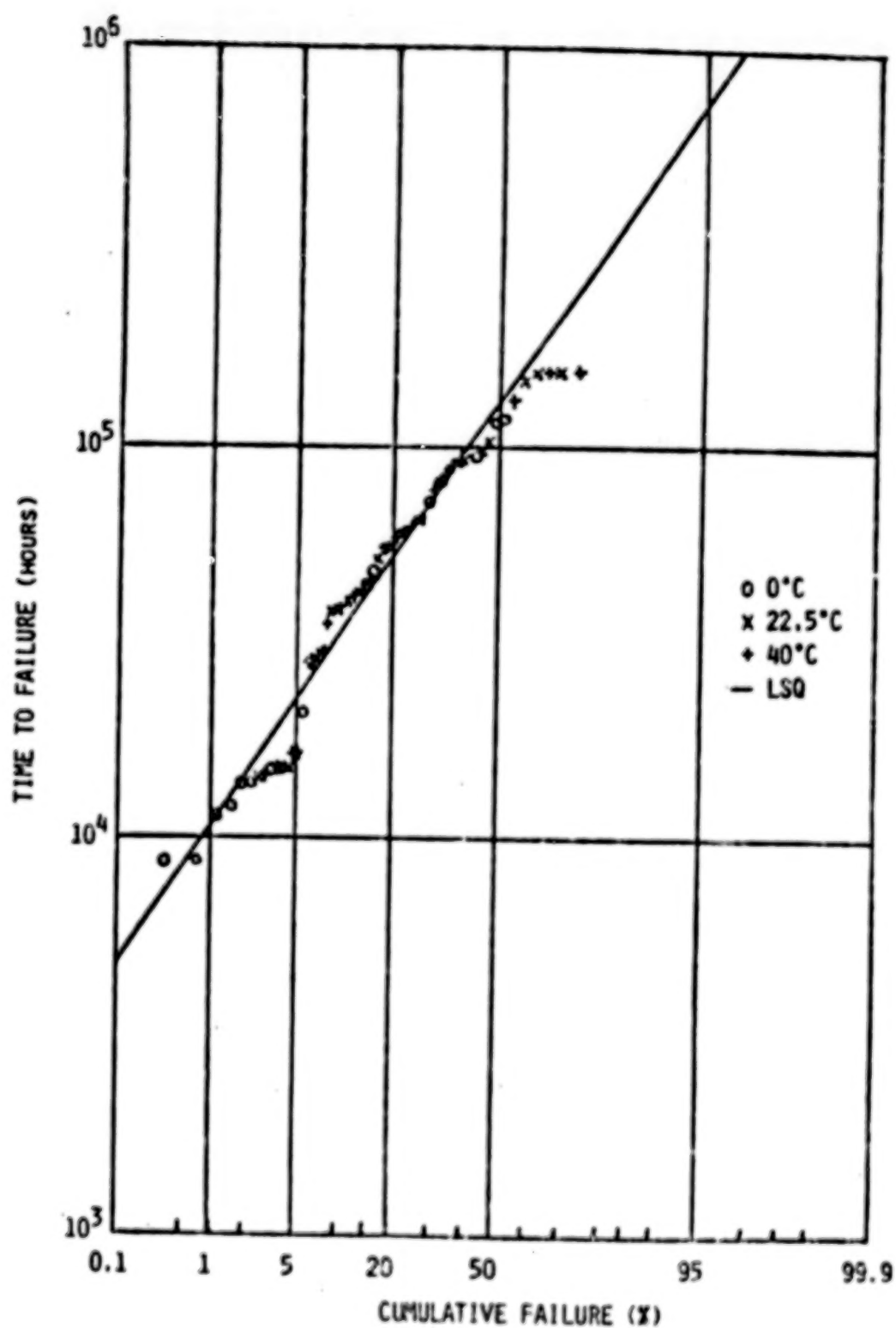
CRANE DATA BASE ON GENERAL ELECTRIC
PRISMATIC AEROSPACE NICKEL-CADMIUM CELLS

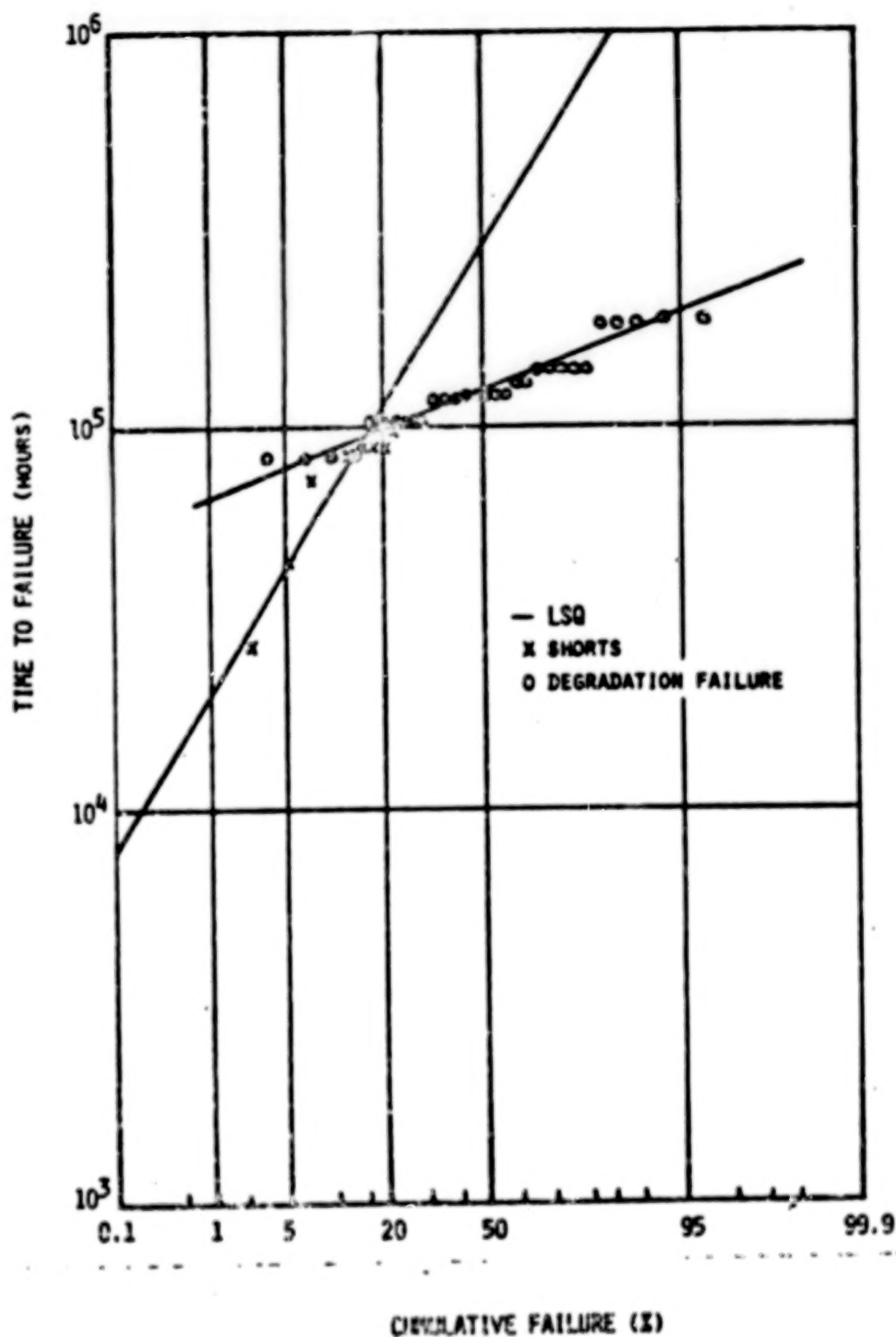
Low earth orbit	304 cells	1963-1977
Geosynchronous orbit	40 cells	1967-1969

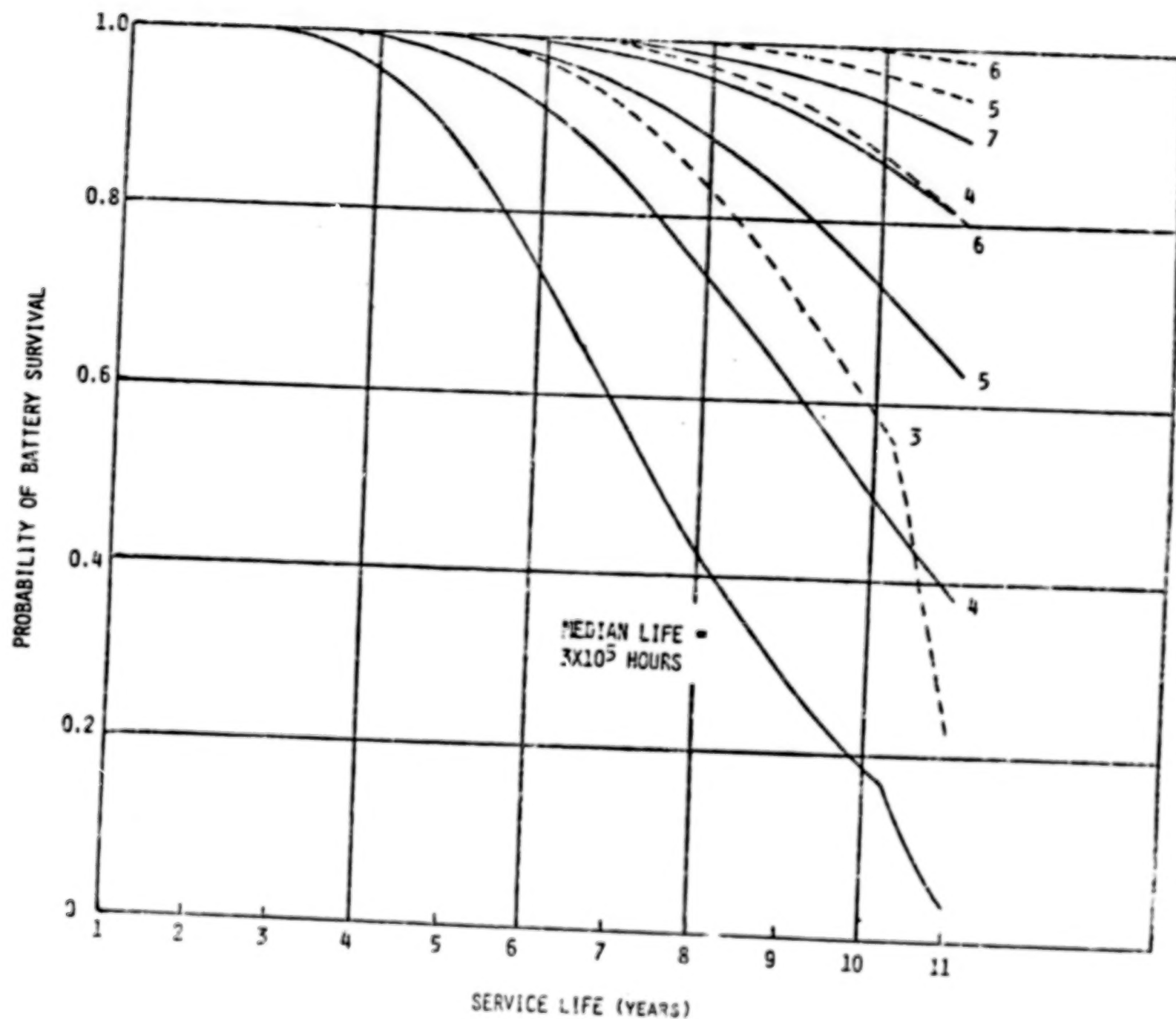
SUMMARY

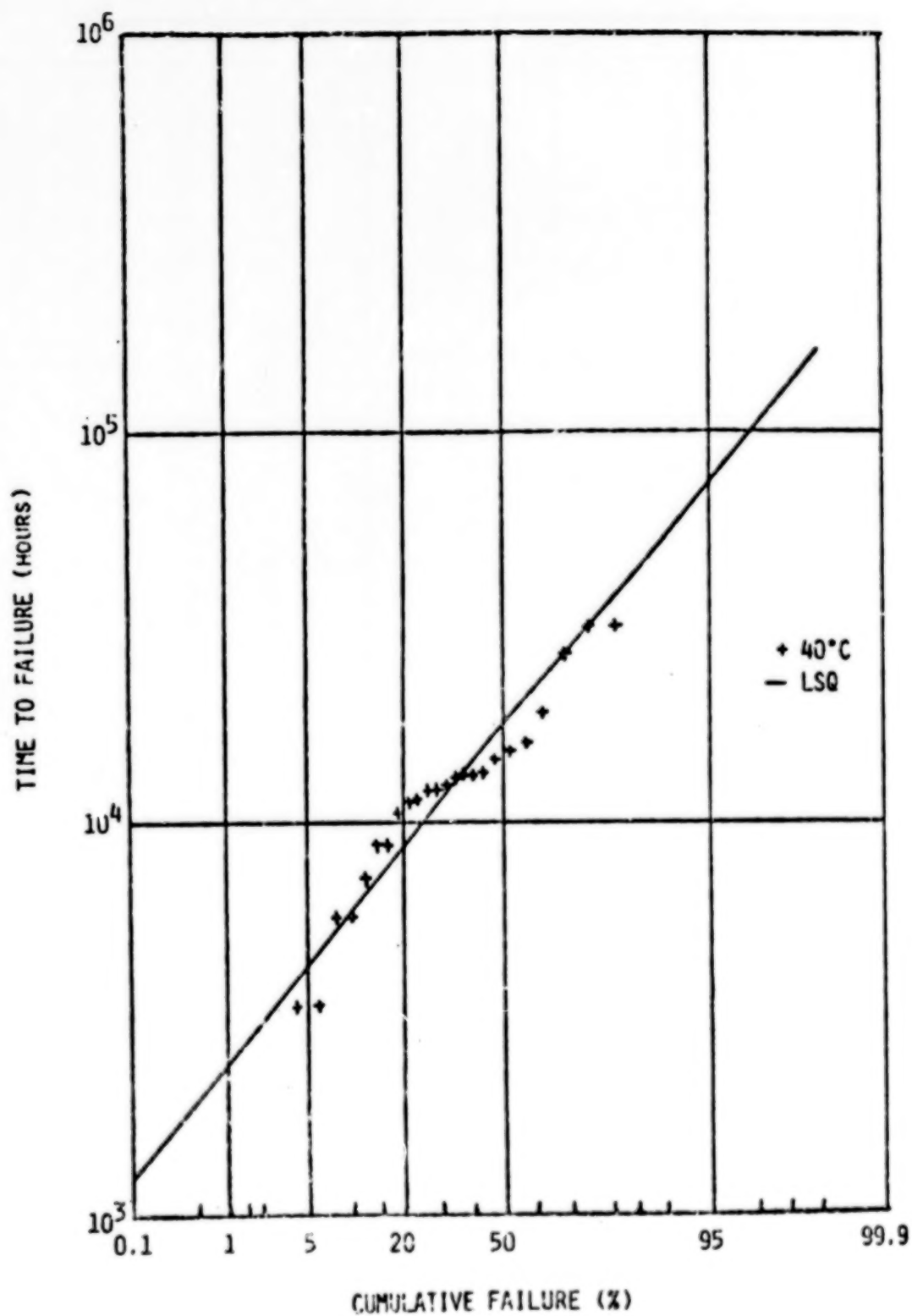
- Later vintage (1978) cells have not been on test at Crane long enough to extrapolate capacity performance.
- Probability of battery survival depends on redundancy and median life.
- Factor of two improvement in median life over pre '69 vintage cells is needed to reach ten-year mission.











ADVANCED NICKEL HYDROGEN
CELL CONFIGURATION STUDY

PRELIMINARY RESULTS

By E. Adler and F. Perez
Hughes Aircraft Company
Space and Communication Group
Technology Division
El Segundo, California

ADVANCED NICKEL HYDROGEN DESIGNS
by Frank Perez

I would like to share something with you. We have been doing a study at Hughes Aircraft concerning large kilowatt hour systems. Yesterday we had a talk from James Masson about the future trends of satellite power systems. Specifically today I am looking at the bipolar design. We have worked on the IPV, the CPV; I will explain this later, and we think that the bipolar design offers improvements in the motherhood statement that was mentioned the first day of this seminar. This work has been funded from NASA/Lewis Research Labs.

We want to provide an evaluation of the current nickel hydrogen cells that we have right now. The IPV, or the Individual Pressure Vessel, is the state of the art right now. At Hughes we have been developing it for 10 years. The present design, 3½ inch cell, has a current limit of 50 ampere-hours. To increase that there are some problems we have to overcome. The CPV is now in the development phases with Gere Hollick and EIC and Yardney. It is in the Dilton phase; I must emphasize, and the bipolar design proposed by NASA last year is just a year old, so the results today are specifically emphasizing the bipolar design.

The nickel hydrogen cell design shows [Figure 2] is state of the art. Its size is 3½ inches which limits it to 50 hours and if we want to make it a larger cell we have to increase the diameter. The probable limits of that are probably 160 ampere IPV cell remaining in the passive cooling mode. That roughly scales to a 5-inch diameter cell. Improvement in the packaging efficiency is the CPV concept [Figure 3]. What we have in the CPV module is IPV stacks. The IPV stacks, as you know, is a parallel connection of electrodes. Positive electrodes are connected with leads to the top portion of the stack and negative electrodes are connected with leads and pulled down to the bottom. So it is a combination connection of paralleling series electrostacking--parallel inside each individual stack, and series connected from one stack to the next. It offers, in the analysis, improvements in packaging and the motherhood statement basically, which is cost, energy density, and specific energy. The bipolar design shown in Figure 6 is made of the electrodes stacked in series; they are inside the stack subassembly. We put several of those on top of each other, put those in a stack subassembly, and put several of them inside the cell--inside the battery. Between each stack subassembly we put a cooling plate. One thing that is a crucial piece of element in the bipolar design is the bipolar plate itself. It serves many purposes. One of them is that it connects electrically one electro pair to the next. The other thing it has to do is isolate the electrolyte in each

ADVANCED NICKEL HYDROGEN DESIGNS

electropair area. It must also offer oxygen recombination in the negative electrode region. The reason why we need an active cooling system is because of the large sizes we imaging in the design. Typically a 45 kilowatt hour battery would scale the 30 inches in diameter. We see in Diagram #5 that the leads are connected from the last electropair, or the last stack of sub-assembly, up to the top positive and negative at the bottom. The coolant system comes in from the top terminal and is distributed in one of four manifolds into the stack subassembly. The coolant comes in from the four tubes I mentioned earlier and it goes into the manifolds. They come down into the cooling plate and it is distributed out through the exit manifold. Gas inlet windows offer the access and excess of the hydrogen gas into the common space of the bipolar vessel. That is another thing I forgot to mention about the bipolar plate. It offers gas excess and access to the negative electrode. It offers all those things besides being structurally sound.

One thing about the bipolar design, we have just looked at it for roughly one-half year now. It is a complicated mechanical design and we have written some computer models of it. I would like to explain briefly the results. I used the units one hour per pound. In Graph #7 cell capacity per volts is plotted. It turns out that cell capacity squared in a series connect the bipolar design and the voltage scale as the stack length. This means you are connecting batteries and electrodes, so it is proportional to the amount of electrodes you connect in series. On the Y axis cell capacity is from 50-424 ampere-hours. Voltage is from 25 volts to 475 volts. On the Z axis is one hour per pound. On the left-hand side the units are 5 to 17.5. On the right-hand side they are 10 to 22.5. It is roughly a 25% increase in going from the normal thickness to the double thickness positive plate. What I mean by that is the normal thickness positive plate is the current manufacturing capability of manufacturing electrodes. Double thickness is twice that. We do not have that now in our manufacturing process anywhere. The reason double thickness is shown on the diagram is because the current conduction paths in the bipolar design are a lot different from the IPV and the CPV modules that we have in the state of the art. Namely that the conduction path in the bipolar plate is actual, so if I take a thickness which is roughly 34 millimeters right not, that is about two orders of magnitude different from the radio conduction paths afforded by the IPV and CPV designs, they are roughly the thickness of the annular region in the stack--about an inch or two.

Let me go briefly to the energy density plot [Figure 8]. Energy density and the units on the Z axis are one hour per cubic inch. The cubic inch represents hexagonal volume which is

ADVANCED NICKEL HYDROGEN DESIGNS

the circumscribed volume of the cell--of the battery. It tapers up in a normal thickness plate to roughly 0.8 watt hours per cubic inch and for the double thickness plate it has a nice plateau as shown on the plot. Comparing the two pilots side by side, just to point out the optimum region, the normal thickness plate shows that the watt hours per pound and the watt hours per hexagonal volume will roughly be at low cell capacity. Low meaning 50-100 cell watts per pound and high voltages. Likewise in the double thickness, because of the plateau region being wider, we have a wide area for optimizing our bipolar cell design.

[Figure 9] Another parameter we vary is the pressure on the packaging factor, the watt hours per cubic inch parameter. We see another improvement if we raise the operating pressure--the limiting pressure of a 1000 psi vessel to a 2000 psi. We see the trend here that the curve slopes up and does not plateau until a higher level. If we can raise that operating pressure, in other words, design the case to withstand 2000 psi, we can shrink the cell down and we do not have to extend it because the pressure might get too high.

A summary at the cell levels (see Diagram 4) for a 150 ampere-hour cell. When comparing side by side the relative sizes of the IPV, the CPV, and the bipolar cell, you see the lower orbit is 1.2 for the IPV. For the CPV the lower orbit is 7.2 and for the bipolar plate we can choose the voltage. We picked an optimum region with 300 volts. Weights are 10, 53, and 2,000, respectively. Specific energy is 17 for the IPV, 20.3 for the CPV, and 20.5 for the bipolar. The energy densities are 0.47, 1.13, and 0.95 for all three. We see the CPV and the bipolar design are comparable at the cell level.

[Figure 11] However, on the systems level if we take a military mission that would need 52 kilowatt hours to the load (I guess these are standard figures or standards requirements for military missions), and a 10% redundancy, it would meet mission requirement if one battery failed--this is a 4-battery system. Each battery would have 125 ampere-hours and 170 nominal voltage. The IPV system would consist of 150 pressure vessels. There is a confusion of cells as a unit of voltage or modules, but there are no modules for CPV and one for the bipolar design.

A weight comparison shows the following [Figure 10]: There is an improvement of roughly 15% between the IPV and the CPV, and there is an improvement of 25% roughly between the IPV and the bipolar design. The reason is because of all the things that are eliminated due to the compact, efficient design of it.

ADVANCED NICKEL HYDROGEN DESIGNS

The reason we have this thermal management is because for large 52 kilowatt hour missions, there is a need to take away the heat actively. We cannot rely on passive cooling anymore. One footnote to this, the IPV design you see in Diagram 4 is an improved version of the standard 3½ inch cell that is currently state of the art. The state of the art cell only gives 1/3 the energy storage and we would need a 30% weight penalty to the 6,500 pounds. So there is more improvement in considering these advanced systems.

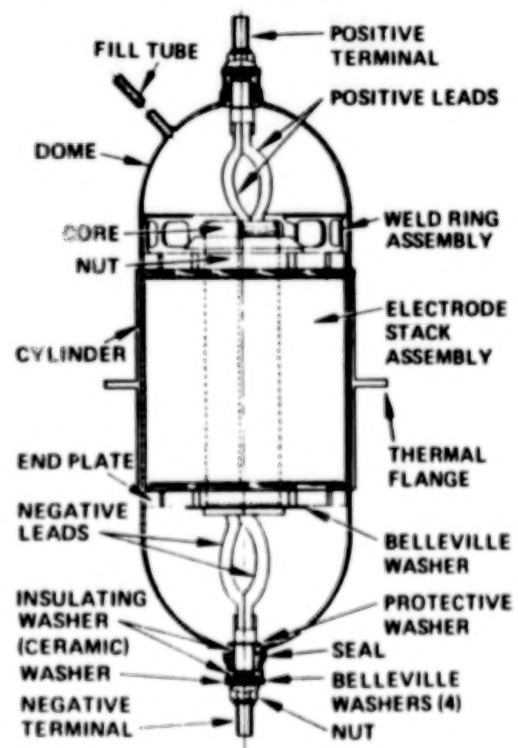
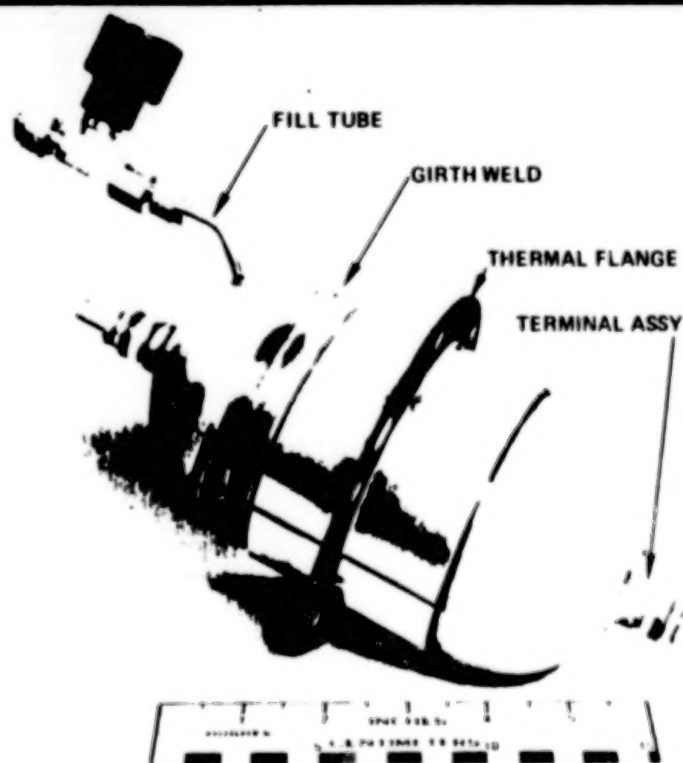
Some things I have not mentioned because of lack of time. I could not dwell on the picture of the bipolar design, but I will include it now. We see that the bipolar design offers the highest payoff due to increased packaging efficiency. Weight savings are 25% in the order, 50% on the volume, and 50%-70% on the cost. The reason for that is less accessories and less parts to make. I forgot to mention that there are some developments or issues that are important in the bipolar design, which are probable to the CPV design. They are the electrolyte management and oxygen management, common to both of those designs. The CPV is underway and it should tell us a few of those issues which can offer a little solution. The final statement is that the bipolar design seems to offer the best potential improvements over both the IPV and the CPV for large capacity systems.

Thank you for your attention.

PROGRAM OBJECTIVES

- **PROVIDE EVALUATION OF CELL CAPABILITIES**
 - IPV**
 - CPV**
 - BIPOLAR**
- **DEFINE BASELINE DESIGN FOR USE IN LARGE ORBITAL PLATFORMS**
- **IDENTIFY DEVELOPMENT REQUIREMENTS**

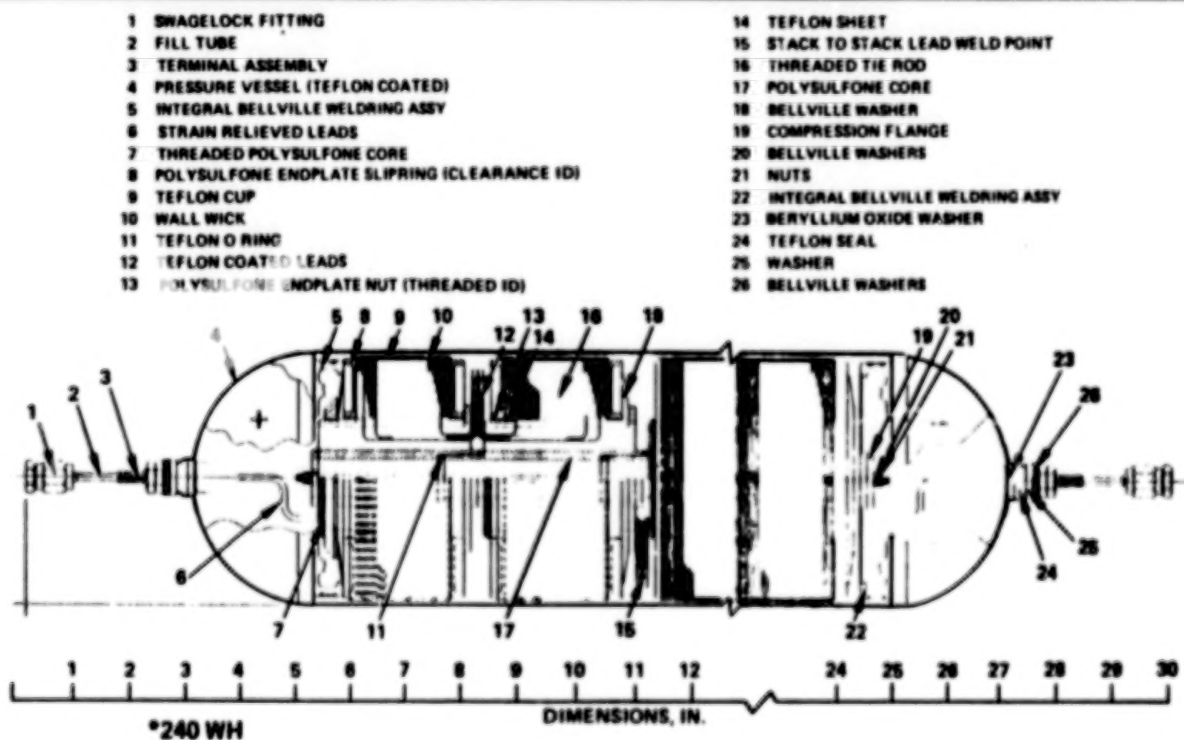
NICKEL-HYDROGEN BATTERY CELL **40 AMPERE HOURS**



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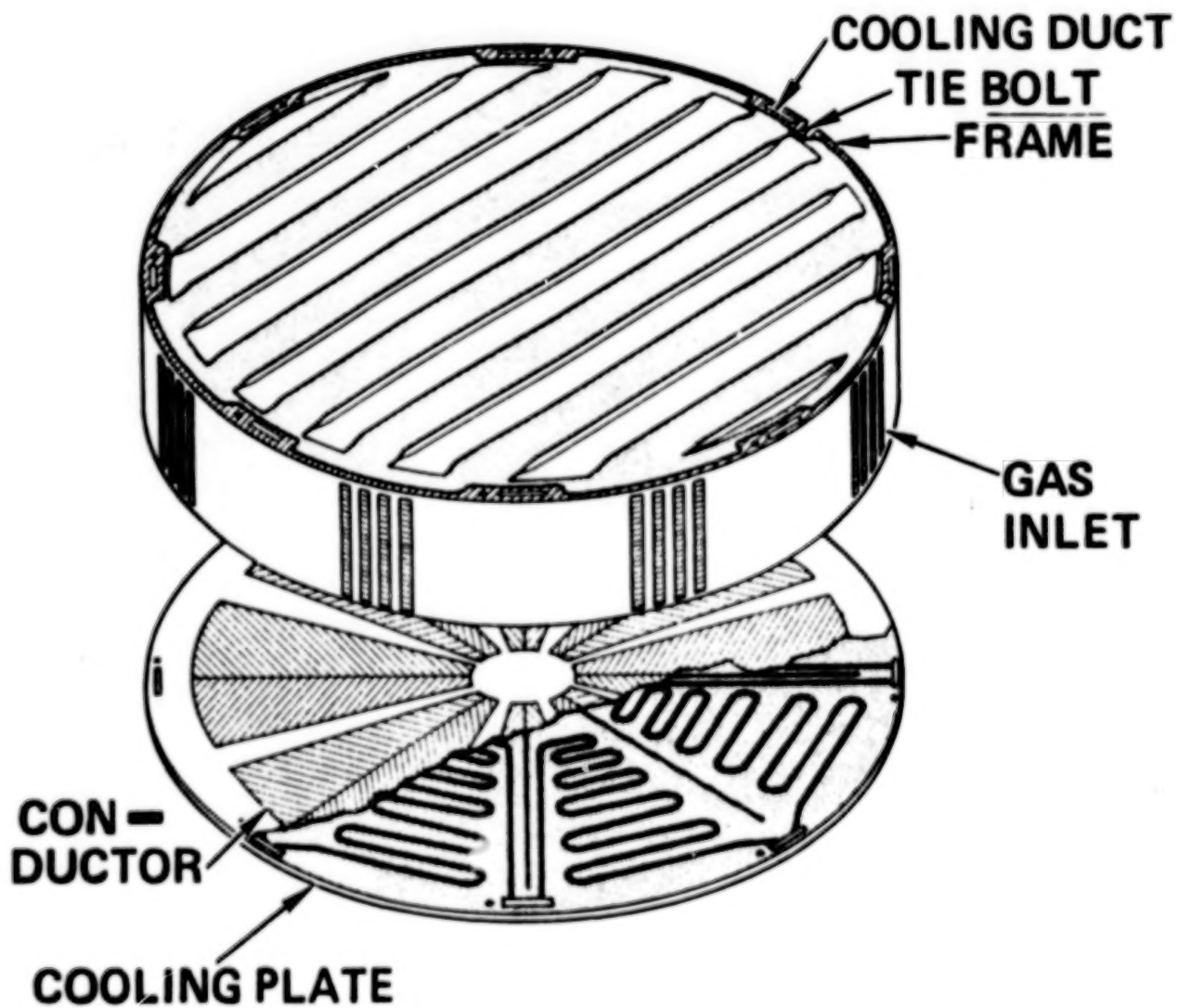
CPV MODULE DESIGN*

OPTION 1



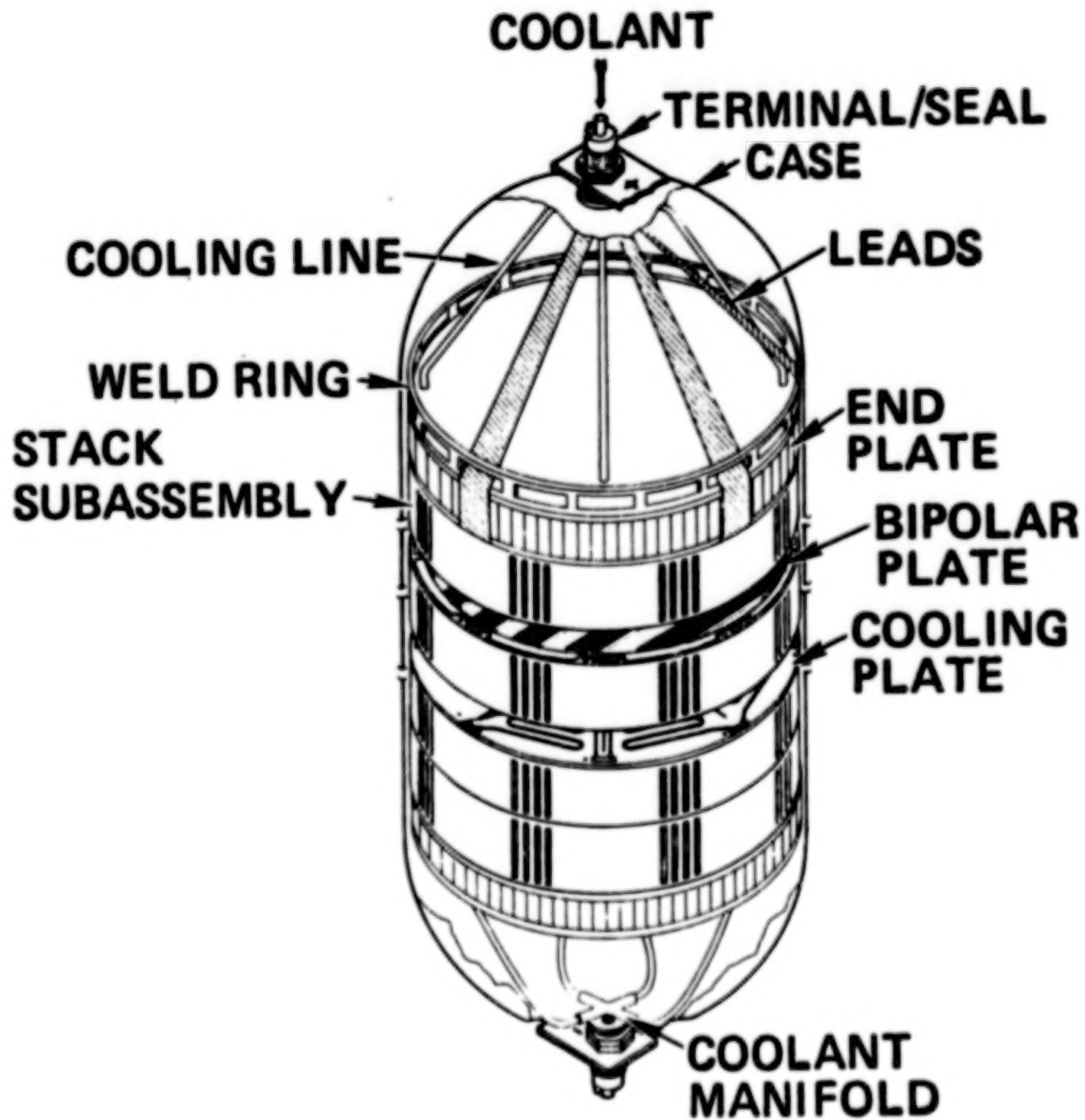
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STACK SUBASSEMBLY



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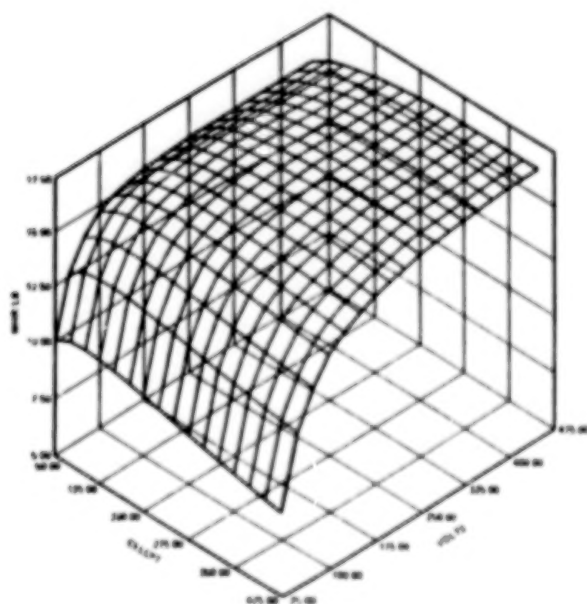
BIPOLAR CELL DESIGN



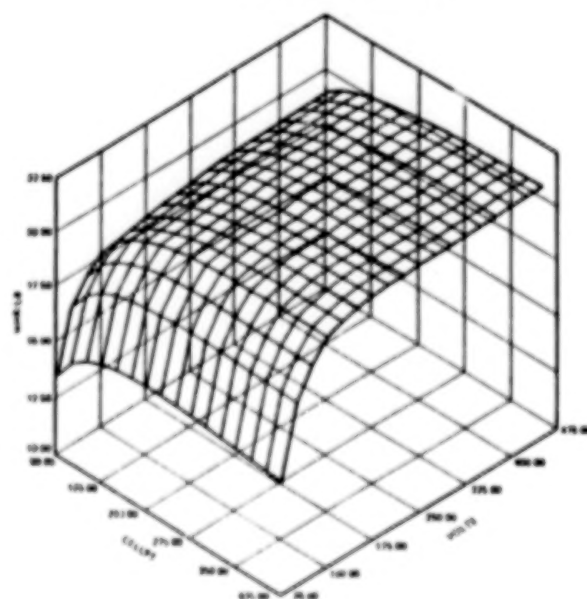
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SPECIFIC ENERGY

NORMAL THICKNESS



DOUBLE THICKNESS

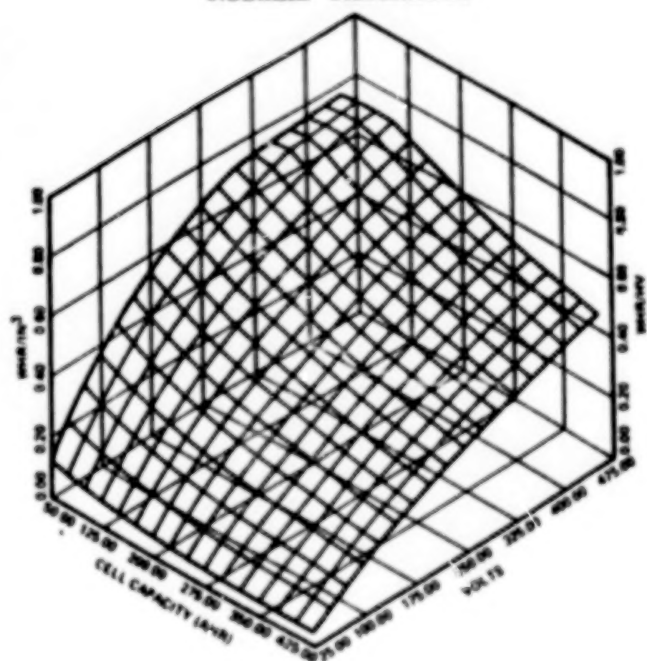


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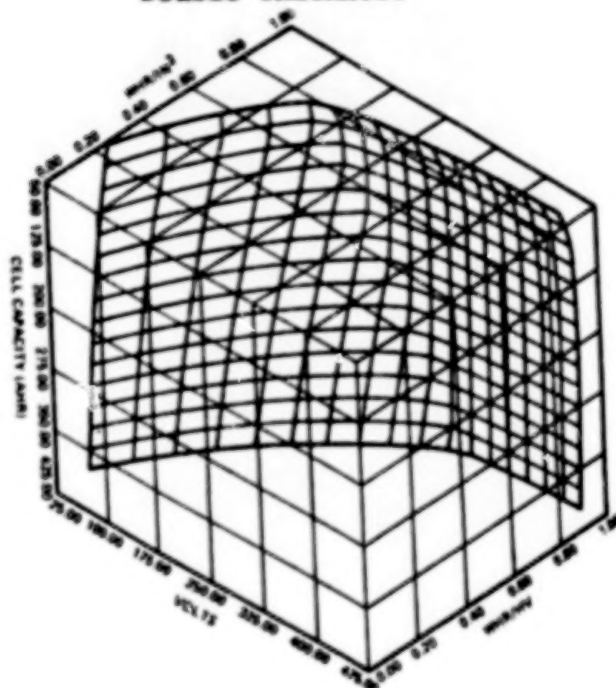
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ENERGY DENSITY

Normal Thickness

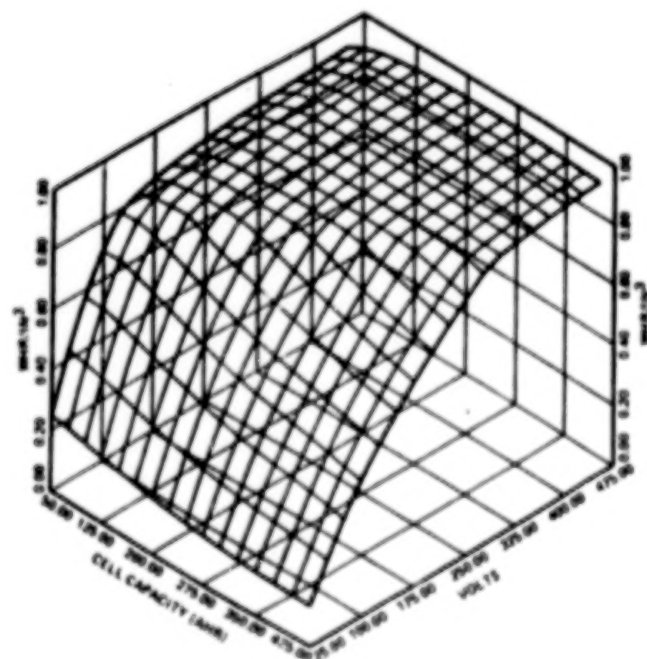


Double Thickness

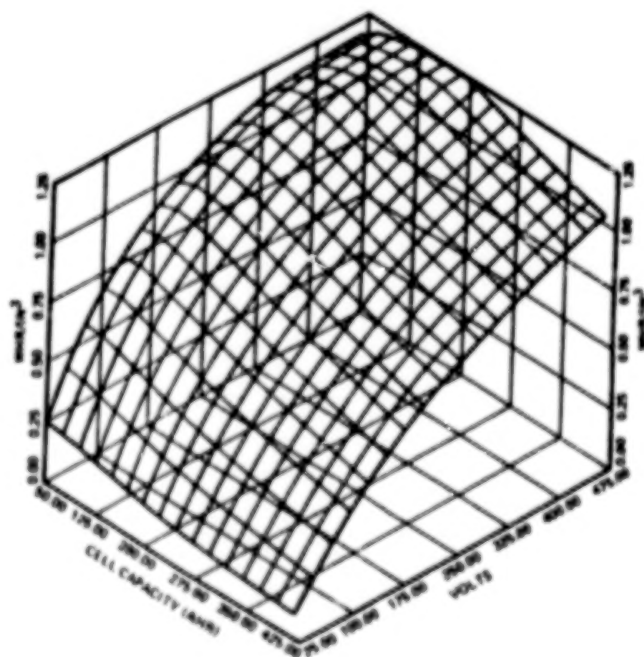


EFFECT OF OPERATING PRESSURE

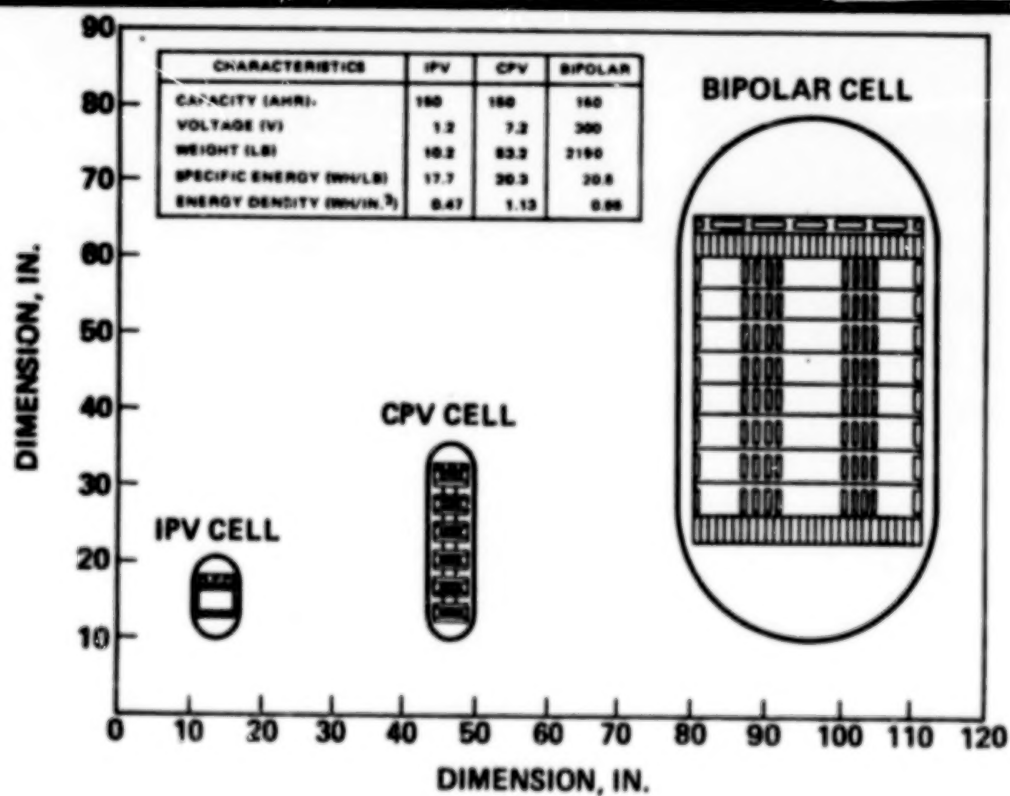
1000 PSI



2000 PSI



CELL COMPARISON



BATTERY DESIGN

	IPV	CPV	BIPOLAR
ENERGY TO LOAD (KWH)	52	52	52
NOMINAL VOLTAGE (V)	170	170	170
NOMINAL DOD (%)	60	60	60
MAX DOD ⁽¹⁾ (%)	80	80	80
INSTALLED CAPACITY (AHR)	500	500	500
NUMBER OF BATTERIES ⁽¹⁾	4	4	4
NUMBER OF CELLS/BATTERY ⁽²⁾	150	150	150
NUMBER OF MODULES/BATTERY	—	25	1

⁽¹⁾ MEETS MISSION REQUIREMENTS WITH A FAILED BATTERY

⁽²⁾ 10% PROVIDED FOR REDUNDANCY

WEIGHT COMPARISON

COMPONENTS	WEIGHT, LB		
	IPV	CPV	BIPOLAR
CELLS	5280	4840	4680
BYPASS	222	37	↓
WIRING	172	29	
ATTACHMENTS	140	24	
INSTRUMENTATION	105	18	
MOUNTING PLATE	202	180	
THERMAL CONTROL	205	205	↓
THERMAL MANAGEMENT	150	150	150
	<u>6476</u>	<u>5483</u>	<u>4830</u>

CONCLUSION

- **ADVANCED CELL DESIGNS OFFER POTENTIAL WEIGHT (25%), VOLUME (50%), AND COST (50 TO 75%) REDUCTIONS COMPARED TO IPV TECHNOLOGY**
- **BIPOLAR CELL DESIGN HAS HIGHEST PAYOFF DUE TO INCREASED PACKAGING EFFICIENCY**
- **CONSIDERABLE DEVELOPMENT WILL BE REQUIRED, TO ASSURE ADEQUATE MECHANICAL DESIGN AND SATISFACTORY ELECTROLYTE AND OXYGEN MANAGEMENT OF ADVANCED BIPOLAR AND CPV CELL DESIGN**

TEST METHODS AND RESULTS OF THE 10-CELL BIPOLAR Ni-H₂ BATTERY

Characterization tests were carried out at three charge levels and four discharge levels. The "c" or capacity of the battery is designated at 6.5 ampere-hours. The recharge ampere-hours was the same for all test conditions, 6.5 A-H, regardless of the discharge capacity removed for any particular discharge rate. Less capacity can be removed at higher discharge rates to the same termination voltage, which was 0.50 volts for the weakest (lowest voltage) cell.

The general trend of efficiencies increases as the charge rate increases as noted in results of the table included in the handout package. The data also indicate the efficiency increases as the discharge rate decreases. This is true; however, efficiencies at the discharge rates of c and 2c are penalized because these cycles received more overcharge than necessary.

The equations used to determine efficiencies are:

$$\frac{I_{\text{out}} \times T_{\text{dis}}}{I_{\text{in}} \times T_{\text{chg}}} \times 100 = \text{ampere hour eff.}$$

$$\frac{P_{\text{out}} \times T_{\text{dis}}}{P_{\text{in}} \times T_{\text{chg}}} \times 100 = \text{watt-hour eff.}$$

where: I = current (amps)
P = power (watts)
T = time (hrs)

The Leo cycling tests were run at a 1 hour charge and half hour discharge. A typical charge/discharge voltage profile of one cell is shown for cycle #66. End of charge voltage is 1.50 volts and end of discharge voltage is 1.18 volts. Testing was terminated at 100 cycles so that a peak power test could be run and one cell removed from the stack for analysis and evaluation. The stack is presently on test (LEO cycles) with nine cells. The components of the removed cell are being evaluated for electrolyte distributions and physical conditions. No problem areas were observed within the cell. Some corrosion was evident external to the cell frame on the bipolar plate. It is presently being analyzed for chemical composition.

The peak power point of the battery was determined by ramping the discharge current via electronic loads until voltage and current crossover occurred. Discharge current at the peak power point was 165 amperes at 6.6 volts at the

battery terminals, thus supplying 1,100 watts of power. This discharge current corresponds to a 25c rate. These results are lowered because only two #14 AWG wires connect each battery end plate to the vessel power terminal which is only rated for 25 amperes, thus significantly increasing power lead resistance.

Conclusions of the results prove favorably on behalf of the first bipolar Ni-H₂ battery. Only good performance and high efficiencies comparable to other Ni-H₂ designs have been observed. The engineering of electrolyte, oxygen and thermal managements become easier tasks by virtue of bipolar battery construction. In addition, peak power and discharge rate capability of bipolar construction make this design very attractive for applications needing this feature in its energy storage system. Bipolar construction also yields higher energy densities than other more conventional designs.

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SUMMARY OF CYCLE TESTING OF BIPOLAR STACK

Charge Rate Discharge Rate	C/4	C/2	C
C/4	93.7 86	97 88	98.3 88
C/2	88.6 81	87 78	93 82
C	88 78	91 80	88 76
2C	86 73	90 76	90 75

GENERAL TRENDS:

1. INCREASED EFF. AT THE "C" RATE CHARGE.
2. INCREASED EFF. AT THE "C/4" RATE DISCHARGE (CONSTANT RECHARGE OF 6.5 A-H)

SUMMARY OF LEO TESTING OF BIPOLAR STACK

0.8C CHARGE RATE

1.5C DISCHARGE RATE

100 CYCLES RUN

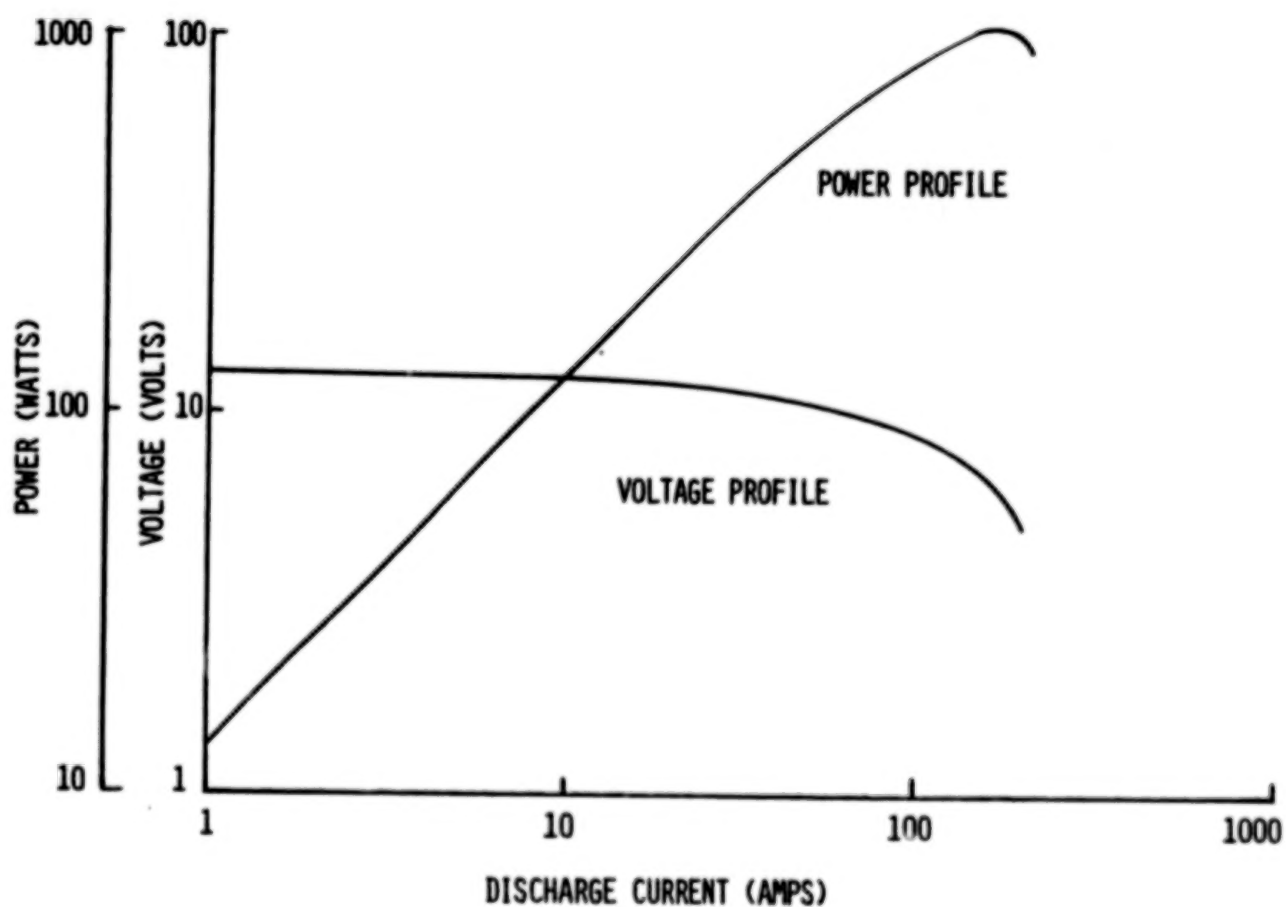
RECHARGE RATIO 1.08

AMP-HOUR EFF. 93%

WATT-HOUR EFF. 81%

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PEAK POWER TEST OF BIPOLAR STACK



CHAIRMAN'S SUMMARY

Luther W. Slifer, Jr.
Goddard Space Flight Center

The hour is getting very late so let me conclude this session by summarizing the presentations and discussions.

We can conclude that:

1. There is a place for both Ni-H₂ and Ni-Cd cells.
2. For higher power systems Ni-H₂ appears to have an advantage over Ni-Cd, while Ni-Cd appears to hold the advantage for low power systems.
3. The advantage cross-over occurs somewhere in the range of 1 to 3 kilowatts.
4. Ni-H₂ cells have been shown to be flightworthy for geosynchronous orbit and will soon be flown there.
5. Flightworthiness of Ni-H₂ cells in low earth orbit remains to be shown. For these applications, the data base is negligible and is needed, critically needed.

SESSION V

DISCUSSION

OPENING REMARKS:

Lou:

Panel today consists of 4 persons:

Jim Dunlop, Comsat

Fred Betz, NRL

Steve Standnick, Hughes Aircraft

Joe Lackner, Defense Research Board, Canada

Slifer, GSFC: First question is, is nickel-hydrogen imaginary? In terms of spare power applications is it real or is there going to be a serious problem? Can nickel-hydrogen compete with nickel-cadmium? I think that's a question that's very important and that we have to face up to. The third major question is why aren't we flying nickel-hydrogen? I think we have to really face up to these questions. Related to that question is, what is a space worthy nickel-hydrogen cell? What do we know about the real performance of the cells? There are data for early generation cells that have been in literature, are they valid for current general cells, is there data and how valuable is it, how extensive is it for current design? We have to separate real performance from projected performance. We have to ask ourselves how good are the projections and how and when will these projections be accomplished? Finally, and this is a key question for systems engineering, where is the nickel-hydrogen cell data base?

Q. Stockel, Comsat: Joe, I'd be interested to know how you made those measurements of the concentration variations between charge and discharge?

A. Dunlop, Comsat: I'd be glad to answer that. I might ask Joe Stockel to answer. What we did was we took from the Landsat 5 program two cells from this lot six group and we used a normal analysis procedure for one cell which we've done many times, which is to discharge the cell down to zero volts, cut the cell open, take the electrode stack out, put it into a nickel-cadmium, extract the electrolyte, dry the stack up, make a weight difference and do the entire analysis similar to the way people have been doing analysis for both nickel-hydrogen and nickel-cadmium cells for probably the last ten years. Based on that information you can determine the KOH and carbonate concentrations of your electrolyte. We've done that many numbers of times in the program. Recently, we decided to try and do a cell in the charge state where we took the cell and fully charged it and the problem with doing that cell in a fully charged state, if you go into

the literature, is people feel that the reduced form of the nickel-hydroxide is fairly stable, but the charged form of the nickel-hydroxide is more stable and it's been more difficult to get a good evaluation. Nevertheless, we took the cell and charged it, took it out and did the same kind of analysis. What we found was that the electrolyte concentration agreed with the electrolyte concentration that we thought it should be, which is 31%.

We got a significant difference in the amount of water and if you look at McArthur's expressions here and you make a comparison between the charge and discharge state and you connect the amount of water in KOH concentration charges, you get reasonably good correlations. We've got what we think is excellent correlation in charge of the water content. We've got fairly close concentration, within a few grams to the KOH concentration that we expected.

Q. Rampel, GE: It should be pointed out that the comparisons you made between nickel-cadmium and nickel-hydrogen is, which would chemically produce positives in the nickel cadmium? It would be presumed that the ED electrodes would improve nickel-cadmium at least to the point of producing non-swelling and lessen electrolyte redistribution.

A. Stockel, Comsat: Right! Absolutely right.

COMMENT:

Gaston, RCA: In light with Jim's comment, RCA has two current spacecraft programs which are using nickel-hydrogen, it's the GT&E, and Star Program Communication Satellite. The first launches we scheduled for both programs are in the Spring of 84 and the batteries will go into acceptance test shortly. Thirty ampere hours for the GT&E program 40 ampere hours for the other program.

Q. Sullivan, APL: Fred could you say a few words about the charge control system that you used if any?

A. Betz, NRL: The charge control on TS2? Yes, we had four selectable

temperature limits 14°C, 18°C, 21°C the battery would normally overcharge in the 12°-15°C degree during celcius period. When we went into eclipsing battery, temperature would rise, subsequently battery temperature. When you came out and started charging at the normal rate you were efficiently charging, battery temperature would fall below the set temperature, and we would select the set temperature to make sure it fell below it. Then it would have to rise back up and hit the set temperature to turn off it's normal charge and go to a trickle charge.

Q. Sullivan, APL: Did you measure the temperature directly on the battery?

A. Betz, NRL: Directly on the battery.

Q. Lurie, TRW: You identified openness as the significant mode. Have you ever encountered voltage degradation of sorts?

A. Betz, NRL: Not on NTS 2. We had no cells that were ever identified as shorted; we had no cells that opened. The voltage degradation that we do see has not been anywhere near the kind of voltage degradation that we saw in nickel-cadmium. I just discharged the nickel-cadmium cells after 10 thousand cycles they were almost at 1 volt at 40% depth of discharge. They persisted between 1.05 and 9 volts for another 40-45 minutes. Nickel-hydrogen does not do that.

Q. Lurie, TRW: What about the voltage degradation in the shorts that have been seen in general. Don't they count as possible modes of failure?

A. Betz, NRL: A shorted cell, for instance in the configuration that we flew in NTS 2 would not have effected performance substantially. We would have increased the current slightly because it's a constant power system and the voltage of the battery system would have indeed been a lost cell voltage plus roughly 2/10 of the reverse potentially and it would not have affected the performance of the system depth of discharge only increases by 1/4.

COMMENT

Thierfelder, GE: Well, Fred, being completely objective and unbiased like you are, you got my attention when you mentioned the GTS program so I wanted to point out to everyone that NTS is part of GTS and Navstar satellites, at the same time that the one NTS was orbitry 1 nickel-hydrogen battery six Navstar satellites were orbitry 16 nickel-cadmium batteries in a period of five years. There's been no problem with those 18 batteries. So you may be equal to but so far not proved superior.

Q. Halpert, GSFC: Fred you mentioned the fact that what sounded like

it was very bad for the voltage of a cell to be down around one volt per cell during that second plateau. But if the power system can utilize it at that voltage level, for example our MPS, we can operate at 22 volts of battery so it really doesn't present a problem.

- A. Betz, NRL: No, in fact, and I would concur you can find the ampere hour capacity there or very little loss in ampere hour capacity. All you've lost is some watt hours. I think it would be more serious with a constant power type of system that we used on NTS 2. Okay?

We're running over, let's go on.

- Q. Hafen, Lockheed: Steve you said you were going to address a question of life can you do that?

- Q. Standnick, Hughes: Of Life?

- A. Hafen, Lockheed: Right?

- A. Standnick, Hughes: Well, we have life tests that are similar to the ones you've seen today. We have real time synchronous life tests that are going into their 11th and 12th season. We have very little voltage degradation after the first few seasons. In terms of calendar life, that's about the extent of the basis we have. We have five or less years of real time life tests that Jim Dunlop has been presenting for years and years. We've showed that we have maybe seven or eight years of calendar life.

You look at degradation mechanisms of nickel-hydrogen cells and you find that most of the ones that are calendar life related don't exist for nickel-hydrogen cells, you don't have re-crystallization of the negative, you don't have degradation of the separators and you don't have electrolyte starvation. The only thing that happens in a nickel-hydrogen cell is slowly over the years your positive electrode starts degrading and after looking carefully at the degradation mechanisms you decide that they are due to the swelling and shrinking of the active material as a function of the cycling and the re-orientation of the crystals on the positive electrodes and extrusion of the active material. Those things are more dependant on cycles and depth of discharge than they are on calendar life. So we really feel confident that the nickel-hydrogen battery is going to last for 10 years and maybe a lot longer than that. We really haven't found a life limiting time for the nickel-hydrogen battery in terms of cycles in lower earth orbit. We demonstrated eight 10,000 cycles at 80% depth of discharge in lower earth orbit.

- Q. Milden, Aerospace: If you expand your trade off study to the entire power subsystem, is nickel-hydrogen still advantageous,

including array and all associated in electronic boxes?

- A. Standnick, Hughes: They really turn out to be almost the same in nickel-hydrogen as nickel-cadmium quite honestly. With most systems you can unplug your nickel-cadmium battery, plug in your nickel-hydrogen and everything would work just fine. That includes all the parameters - such as - well anything. Almost any charge system that will work with a nickel-cadmium will work with a nickel-hydrogen. The arrays are the same and a lot of the charge and discharge electronics are the same. There really isn't much of a difference.
- Q. Sieger, Sieger Associates: I have a question for Jim Dunlop. I noticed that on the Land-Sat 4 that you showed an 89% center perocity and knowing the characteristics of that I would kind of suspect there may have been corrosion during the impregnation process. Is that so?
- A. Dunlop, Comsat: Yes, that's correct. And I guess there isn't much more to say about that. There is definitely less corrosion that occurs when you do the electro-chemical impregnation process and typically a comprable electrode chemical process would have about 4% difference in perocity.
- Q. Maurer, Bell Labs: I'd like to ask the nickel-hydrogen people a little bit here . It seems that all of the nickel-cadmium falons are out in the public record and the nickel-hydrogen people have been working away in their labs and running tests, but we haven't seen all the data like we've seen all the data on nickel-cadmium. We just heard Sullivan's talk where we've seen what size data base we need to get to statistically sound evidence, that a battery of some appreciable number of cells will last ten years in any kind of use mode. So you need a large data base to predict shortings. And isn't it true that there have been a considerable number of nickel-hydrogen problems that haven't really been talked about in this meeting? For example, aren't all those nickel-hydrogen cells that were distributed by the Air Force a few years back - haven't all those failed by shortings? And isn't there a problem with nickel-hydrogen over a gradual increase--the discharge and then the charge pressures caused by various things going on inside the cell like corrosion of the positive and things of this sort that perhaps we simply haven't had enough testing, enough cells made to really tell us what the overall reliability of that system is?
- A. Standnick, Hughes: I guess if you are discussing failure of cells, I suppose every cell eventually fails by shorting and when you run them in lower earth orbit for, I don't know how many cycles, somewhere between three and ten thousand cycles at 80% DOD and they

short that is indeed a failure. However, it's a pretty impressive failure by a lot of peoples standards. Regarding the question of the statistical data base, certainly there is not a data base on nickel-hydrogen cells that would establish a statistical projection of the life of any cell. It's probably also true that on any specific nickel-cadmium design, at the time that you fly it, there is also not a statistically significant data base, because in each program we change the design of nickel-cadmium cells sufficiently to probably invalidate our existing data base. So really what we do is try to understand the failure mechanisms as best we can and we go on to accelerated testing of life projections based on failure mechanisms. On that basis there is probably as good as understanding of the characteristics of nickel-hydrogen as there is of nickel-cadmium at this time.

COMMENT

Betz, NRL: I would say there are two elements that have been important for Hughes in deciding to use nickel-hydrogen where we've decided to use it. On commercial programs typically the advantages have been weight and cost and we really haven't realized the cost advantage although we've projected a cost savings even on Land-Sat 6 of using nickel-hydrogen over nickel-cadmium. But there was a weight advantage which was probably about 50 or 60 pounds. And if you can put my channels on by saving 50 or 60 pounds you can earn more revenues and have a better spacecraft. In the military program the primary drivers were used as a development tool to put a battery which does not necessarily have any drivers but is clearly a better battery, for use later on in follow up programs which would be in the higher power range; the 1-3 kilowatt range. And by using it in earlier military programs you have it developed and available for follow-up type programs. So there really were two motivations somewhat separate.

- Q. Dunlop, Comsat: In respect to nickel-hydrogen, I think it's obvious from the figures that Steve put out that around 142 kilowatts to three kilowatts you will have to get away from it and get into another power system strictly on energy density. And we do know, although we may not be using it now. Unless we get a handle on it now and build up that data base, we won't be prepared and that's why, believe it or not, we really do have an interest in nickel-hydrogen.
- A. Standnick, Hughes: Just a quick statement in response to one of Dean's questions that didn't get answered. Is pressure growth on nickel-hydrogen batteries, and I must say that on the NTS 2, I've got looked at that specifically to see what growth we've had in pressure. Joe might have the answer on top of his head, but if my recollection is correct I don't think our pressure growth has exceeded ten percent in the past years.

Q. Lackner, DRB: Is anyone planning on using nickel-hydrogen in low earth orbit in a manner that they will get out of it what you say are the advantages? One of the thoughts I have, for example, is we say it's better when you get in a large power area. There's some work by TRW where nickel-hydrogen is base lined, but it's going to be used under conditions where you only go to 35% depth of discharge and you replace it every three years or so using the shuttle. So I'm wondering where is the real value in the nickel-hydrogen battery - especially for low earth orbit. I think when we talk about long life we are talking about geosynchronous.

A. Standnick, Hughes: The shuttle has an awful lot of limitations other than 150 nautical miles and we'd like to use that orbit. It's a very convenient thing if you're somewhere in the those 800 or 600 nautical miles. Replacement is still a problem. We at NRC do have an active program combining nickel-hydrogen in a full tolerant battery concept. I think for near earth application we don't know where it's gonna happen because there is a lot of work to be done. But I see replacing redundant nickel-cadmium batteries and changing the redundant cells or having the capability to merely eliminate the fail cell and continue operating. What you do with that mechanism is not united by the first cell failure but you're united by the population system. And I foresee higher density utilization, maybe for nickel-hydrogen, certainly 40% discharge for five to six year near earth mission. And we're interested in five year missions in near earth or more, not the two to three year mission necessarily.

COMMENT

Betz, NRL: I think a factor involved with the lack of lower earth orbit missions using nickel-hydrogen batteries is probably due to the fact that many of the prime contractors who are flying low earth orbit missions are not the same ones that have been developing nickel-hydrogen. It just takes awhile for the technology to transfer over, and I expect at sometime there will be more low earth orbit missions using nickel-hydrogen batteries.

A. Schoenfeld, TRW: I'd like to respond to Lou's question regarding the TRW study and also some of the discussions of the advance of nickel-hydrogen and nickel-cadmium in the shuttle area. There is an advance for synchronous orbit. Because of the IUS we're limited in getting up from low earth orbit to synchronous orbit. Instead we can gain advance by reducing the weight of the battery by going to nickel-hydrogen. Then I think nickel-hydrogen systems, especially in larger kilowatt ranges like it was pointed out by Steve, will gain popularity. As far as Jones' question was concerned in low earth

orbit I don't see a weight problem in short term spacecraft. You asked a question, why did the TRW study recommend 33% depth of discharge? As you have noted, theory was presented that we really only have 8,000 hours of life on low earth orbit nickel-hydrogen applications, so we are really limited to one and one-half at this time. At least there's no data that shows that we have longer life nickel-hydrogen at low earth orbit at 18% depth of discharge. You minimize the cost of the battery because you have to re-supply it less often.

Q. Milden, Aerospace Corporation: A question for Steve primarily. Since you folks are not in the near earth orbit business, what's your policy on technology transfer and supply and cell technology to go to war in that business in the military vain?

A. Standnick, Hughes: If requested by the military we will sell cells to any government program.

COMMENT:

Ritterman, TRW: I'd like to make an addition to Art's comment. The projection was based on some data I had gathered and that was for cells manufactured in 76,77,78, and at a seven year life I would think that 33% would probably be longer today.

Q. Halpert, GSFC: I guess one of the concerns we have is with the extreme interest in nickel-hydrogen systems. There are people who feel like all nickel-cadmium cells will be out for spare use in the near future and everything will be turned over to nickel-hydrogen. I'd like to say, Fred has already said it, that there are times when you are going to use nickel-cadmium and I think what we need to do is when we talk about nickel-hydrogen vs. nickel-cadmium, make sure we are talking about the particular application and why the need of the nickel-hydrogen so we don't oversell the cause and have people turned off on nickel-cadmium.

A. Dunlop, Comsat: I'll make a comment on that. I think that the nickel-cadmium battery has improved fantastically since I entered the business in 1925, no fault of mine. I really probably didn't contribute to that effort. The nickel-cadmium system is an extraordinary, dependable and reliable system and I don't think anything that nickel-hydrogen is doing takes anything away from nickel-cadmium. I believe truly that we will be using nickel-cadmium systems for a long time for many applications. There are applications where nickel-hydrogen truly is superior and really will be used on it's own merits.

COMMENT

Schoenfeld, TRW: I would like a second to support that statement. As a matter of fact, Dunlop mentioned one of the motivations for switching from nickel-cadmium to nickel-hydrogen was that there are only two big problems between TWT's and batteries. And our assessment at TRW at this time is that failure in nickel-cadmium batteries is associated with mismanagement, the charge and discharge cycles were improperly done. I think that nickel-cadmium at this time is mature and the cells are good and unless there's a reason to switch we should stay with nickel-cadmium.

- Q. Unidentified: This is a question for Mr. O'Sullivan from Bell Labs where at his session we couldn't ask questions. What are the sigmas for your curves and on the two Geo distributions, what were the slopes on those?
- A. O'Sullivan, Bell Labs: The slopes in low earth orbit were ranged from .9 to 1.4 of 1.06 for shorting, and geo-synchronous the shorting was 1.14 and the capacity degradation was .29. Generally the correlation coefficients range from .91 in geosynchronous to .98 in low earth orbit.
- Q. Unidentified: A nickel-hydrogen spinoff that we are applying in nickel-cadmium is to incorporate improved positive electrodes. The positive electrodes have a much higher utilization and decrease swelling and another thing we've removed an awful lot of weight. For example, for 50 ampere hour cells we now have light weight 50 ampere hour cells. We removed about one pound from a 50 ampere hour cell. The 15 - 35 ampere hour cell is a light weight cell using a 12 mil case. We can also reduce weight on that cell now-a-days.
- Q. Puglisi, Yardney: I'd like to ask a question concerning Dr. Lim's paper. When you gave the loading levels in groups per CC were those strictly the nickel-hydroxide or did you include the cobalt that may have been added?
- A. Lim, Hughes: That's weight pick up during loading, so it includes cobalt.
- Q. Puglisi, Yardney: Second question: You seemed to say you were going with the dry center, is there a reason that you can discuss why you selected that as your baseline?
- A. Lim, Hughes: We have to select one technology data. We were given unlimited choices of variation for the scope of the program and we cannot use them all, and dry center is better in various aspects in con-

trolling in center fabrication. So we just have chosen the dry technology as a baseline and also the dry center as the baseline for the Air Force.

- Q. Puglisi, Yardney: Just a comment on another point. The efficiency that you were talking about, the loading level, the one which you showed a figure for which described efficiency as a function of the loading level. I think you had a lot of scatter in that figure if I recall correctly.
- A. Lim, Hughes: That's right. I showed two figures. One is before stress tests which measures the capacity divided by theoretical capacity which is based on the loading and electron charge, and the second one is the same utilization after 200 cycle stress tests.

I think with regard to today's questions, what has been described would first lead to the statement that nickel-hydrogen and nickel-cadmium both have their places, and it's up to proper engineering to select those places. There will be undefined areas of overlap. It appears that for large powered systems in the one to three kilowatt range is where the cross-over occurs between nickel-hydrogen and nickel-cadmium. The data base is available for nickel-hydrogen to the extent that there are firm commitments for using nickel-hydrogen in geosynchronous orbit. But it is not available for nickel-hydrogen to the extent that there are firm commitments for using nickel-hydrogen in geosynchronous orbit. I think that is an area particularly in the era of shuttle, while we're considering things like space stations and large power systems. I think that's an area that really needs some work. With that I'll close this session.

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16. Abstract <p>This document contains the proceedings of the 15th Annual Battery Workshop held at Goddard Space Flight Center, Greenbelt, Maryland on November 16 to 18, 1982. The Workshop was attended by manufacturers, users and government representatives interested in the latest results in battery technology as they relate to high reliability operations and aerospace use. The subjects covered included Lithium Cell and Battery Safety Developments, Mathematical Modelling, Charge Control of Aerospace Power Systems, the Application of Nickel Hydrogen Cells/Batteries vis-a-vis Nickel Cadmium Cells/Batteries.</p> <p>This Workshop comprised five separate Panel discussions on these subjects. This document contains the formal papers presented in each session, questions and answers, and a transcript of the discussion/comments by the attendees and panel members.</p>					
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